



## Absorption spectra in the vacuum ultraviolet region of small molecules in condensed phases

Hsiao-Chi Lu<sup>a,b</sup>, Hong-Kai Chen<sup>a</sup>, Bing-Ming Cheng<sup>a,\*</sup>, J.F. Ogilvie<sup>c,\*</sup>

<sup>a</sup> National Synchrotron Radiation Research Center, 101 Hsinn-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan

<sup>b</sup> Department of Material Science and Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan

<sup>c</sup> Escuela de Química, Universidad de Costa Rica, Ciudad Universitaria Rodrigo Facio, San Pedro de Montes de Oca, San Jose 2060, Costa Rica

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### ABSTRACT

With radiation from a synchrotron we measured the spectra of several small molecular species, in the solid phase at 10 K, either pure – O<sub>2</sub>, NO, CO<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>O and NH<sub>3</sub> – or, for NH<sub>3</sub>, also dispersed in Ar at molar ratio 1/250, from the onset of absorption in the ultraviolet region until the limits of transmission by crystalline LiF or solid Ar. In a quantitative treatment of spectral data, we fitted the total absorption profile divided by wavenumber to Gaussian curves of minimal number, and made tentative assignments of electronic transitions and vibrational structure by comparison with spectra of gaseous species. These results illuminate the nature of electronic spectra of samples in solid phases in the vacuum ultraviolet region.

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### 1. Introduction

Despite the much enhanced experimental difficulty in the vacuum ultraviolet region, early molecular absorption spectra of gaseous samples provided qualitative information about electronic transitions of simple molecules, like the more thorough analysis of spectra in the visible and near ultraviolet regions [1–3], but little quantitative information is available about the spectra of these compounds in condensed phases. The reported spectra suffer from then challenging experimental conditions; compare, for instance, spectra of solid H<sub>2</sub>O and NH<sub>3</sub> [4] with our spectra here. Especially with major facilities such as electron accelerators or synchrotrons that provide intense radiation with a continuous span, quantitative measurements of both wave length or wavenumber and intensity are at present achievable for compounds such as those of astrophysical interest. In some cases already known, prominent features of the spectrum of a sample in a condensed phase somewhat resemble those for the same compound in the gaseous phase: for instance, for CO [5] in the region of its first intense absorption system in the vacuum ultraviolet region, the pronounced vibrational structure of a gaseous sample persists on dispersion of CO in solid Ar or Kr and even for the pure solid phase, although the vibrational structure accompanying electronic transitions of greater energy, like all rotational fine structure, is lost. In contrast, for neat solid methanol

[6] at 10 K there is no trace of the abundant vibrational structure discernible in the spectra of gaseous samples; a semblance of diffuse and overlapping vibrational structure remains in spectra of H<sub>3</sub>COH dispersed in solid argon, but this vibrational structure is better developed for H<sub>3</sub>COH in solid krypton [6]. Although such spectra of molecular absorbers dispersed in solid noble gases attract intrinsic fundamental interest in providing information pertaining to intermolecular interactions and perturbations in such mixed solid environments, the neat solid substances, and their mixtures, are much more useful in modeling the spectra of planetary surfaces.

Applying a synchrotron as a source of radiation and a capability of preparing and handling samples of high chemical purity with devices that provide cooling to at least 10 K, we have recorded the spectra of elemental oxygen O<sub>2</sub> and five simple chemical compounds—nitrogen oxide NO, dinitrogen oxide N<sub>2</sub>O, carbon dioxide CO<sub>2</sub>, water H<sub>2</sub>O and ammonia NH<sub>3</sub>; for the latter we have also recorded the absorption of its dispersion in solid argon at a molar ratio Ar:NH<sub>3</sub> = 250. Some ultraviolet spectra of NH<sub>3</sub> dispersed in solid argon were published many years ago [7], but our refined experimental conditions and advanced procedures of analysis enable an improved treatment to extract quantitative attributes of each contribution to the total absorption. With sophisticated software we fit the spectral profile quantitatively as a sum of Gaussian contributions, each implying a separate electronic or electronic plus vibrational transition. Our analysis of these spectra yields information about the electronic transitions and structures of these molecules in their electronically excited states; we compare our results with published work.

\* Corresponding authors.

E-mail addresses: [bmcheng@nsrrc.org.tw](mailto:bmcheng@nsrrc.org.tw) (B.-M. Cheng), [ogilvie@cecm.sfu.ca](mailto:ogilvie@cecm.sfu.ca) (J.F. Ogilvie).

## 2. Experiments and analysis of data

With a double-beam absorption apparatus as described previously [5,6], we measured optical spectra of condensed samples in absorption in the vacuum ultraviolet region to the limit of transmission of optical components, about wave length 105 nm or wavenumber 95 000  $\text{cm}^{-1}$ . The radiation from a 'high-flux' beam line of a storage ring (1.5 GeV) at the National Synchrotron Radiation Research Center in Taiwan was dispersed with a cylindrical grating monochromator (focal length 6 m). The wave length scale was calibrated with absorption lines of gaseous Xe [8], CO [9,10], O<sub>2</sub> [11], and NO [12–15].

For our measurements on a sample in a condensed phase contained in a conventional cryostat, a gaseous sample was deposited onto a rotatable window (LiF) maintained at 10 K; this window was set to face the gas inlet port. Radiation from the synchrotron then intersected this window at an angle near 45°; the transmitted light impinging onto a window (glass, coated with sodium salicylate) was converted to visible light measured with another photomultiplier. A small fraction of the light beam was reflected from a LiF crystal placed at an angle 45° to the beam line before the cold target, passed one additional LiF window, and then impinged onto a glass window coated with sodium salicylate. The photoluminescent signal therefrom that was subsequently detected with a photomultiplier tube (Hamamatsu R943-02) in a photon-counting mode was employed for normalization. The spectral resolution, limited by the scan steps and constant on a wave length scale, is specified in the caption of each figure; the spectra in figures in this paper are plotted as linear absorbance versus linear wavenumber.

A gaseous mixture of NH<sub>3</sub> with Ar was prepared according to standard manometric procedures, and the other, pure samples were also handled in an ultra-high vacuum system designed for that purpose. The rate of deposition was regulated in a range/nmol s<sup>-1</sup> [20, 120] for pure gases and 740 nmol s<sup>-1</sup> for NH<sub>3</sub> with Ar, as monitored with a flow transducer; the duration/s of deposition was in a range [40, 400] for pure gases and 1800 for NH<sub>3</sub> with Ar. Gases (all acquired from Matheson, USA) O<sub>2</sub> (99.995%), NO (99.995%), CO<sub>2</sub> (99.995%), N<sub>2</sub>O (99.995%) and Ar (99.9999%), with the indicated nominal purities were used as delivered. NH<sub>3</sub> (99.995%) was subjected to freezing at 77 K, pumping and thawing followed by distillation from 206 to 77 K in vacuo. Liquid H<sub>2</sub>O (deionized) was subjected to freezing about 240 K, pumping and thawing, followed by pumping on the liquid sample near 295 K.

In the conduct of our experiments, we recorded first a spectrum for the background that depicts essentially the transmission along the optical path including the cryostat. We then recorded a spectrum for the neat solid molecular species, from which we subtracted the background. From the spectrum of ammonia dispersed in argon as diluent, we likewise subtracted the spectrum of pure argon as background. With appropriate software (OriginPro from OriginLab Corp., USA, and Grams from ThermoGalactic Corp., USA), we converted the measured spectra to a scale linear in wavenumber; to eliminate the frequency factor from absorption intensity, we divided the absorbance by the wavenumber at each point to generate a curve that we fitted with Gaussian profiles [6]. In a form of the wavenumber of the centre of each Gaussian curve, the relative stature (net maximum absorbance), the full width at half stature, the relative area and, where appropriate for evident vibrational progressions, the wavenumber separations between adjacent features, quantitative numerical characterization of the absorption appears in Tables 1 and 2 for the various samples that we measured. The width of the features, not the spectral resolution, limits the precision of those measurements; the uncertainty of the central wavenumbers is likely of order 10% of the width in each case. Wavenumbers within parentheses signify not the maximum of an

**Table 1**

Characteristics of Gaussian profiles fitted to spectra of small molecules as a pure solid and, for NH<sub>3</sub>, dispersed in solid argon (molar ratio 250), all samples at 10 K; for NH<sub>3</sub> in Ar intervals  $\Delta\tilde{\nu}$  between successive lines are also listed<sup>a</sup>

$\tilde{\nu}/\text{cm}^{-1}$	Relative stature/ $10^{-6}$ cm	$\delta\tilde{\nu}/\text{cm}^{-1}$	Relative area	$\Delta\tilde{\nu}/\text{cm}^{-1}$
<b>NO</b>				
47 640	29.0	10 044	0.299	
67 460	4.22	16 700	0.075	
(93 400)	8.62	24 200	0.112	
<b>O<sub>2</sub></b>				
58 820	8.42	9725	0.087	
72 335	27.6	13 360	0.392	
<b>CO<sub>2</sub></b>				
54 300	0.019	10 700	0.00021	
70 164	0.364	9375	0.00364	
79 355	1.64	5266	0.00918	
86 433	8.96	1803	0.0172	
88 191	10.5	3743	0.0418	
(93 300)	19.7	7915	0.088	
<b>N<sub>2</sub>O</b>				
55 530	0.390	7350	0.00304	
63 512	0.175	6200	0.00116	
71 596	9.14	4587	0.0446	
76 960	21.8	4225	0.098	
80 000	11.8	5680	0.0713	
88 487	18.5	14 290	0.224	
<b>H<sub>2</sub>O</b>				
64 610	2.27	3207	0.00773	
69 173	12.1	7704	0.0995	
85 540	14.3	22 000	0.269	
(93 410)	4.93	6285	0.0170	
<b>NH<sub>3</sub></b>				
52 570	4.89	3220	0.0168	
55 140	15.8	6800	0.114	
60 030	15.6	10 320	0.171	
81 750	36.7	21 500	0.756	
(93 410)	18.3	9855	0.0975	
<b>NH<sub>3</sub>/Ar</b>				
52 518	0.616	3500	0.00229	
53 739	1.13	1600	0.00192	1221
55 514	3.28	1950	0.00681	1775
57 258	3.89	1760	0.00729	1744
58 984	3.88	1955	0.00808	1726
60 825	2.76	2000	0.00588	1841
62 649	1.68	2000	0.00357	1824
64 548	1.13	2200	0.00264	1899
66 771	0.941	2300	0.00230	2223
68 851	1.03	2000	0.00219	2080
70 695	1.09	1870	0.00217	1844
72 429	0.954	1680	0.00170	1734
74 286	0.777	1957	0.00162	1857
76 141	0.575	939	0.000575	1855
78 194	0.321	643	0.000220	2053
88 440	12.6	19 300	0.187	
92 940	7.20	6400	0.0269	

<sup>a</sup>  $\tilde{\nu}$  denotes a centre of a Gaussian profile fitted to a curve of measured absorbance divided by wavenumber/ $\text{cm}^{-1}$  to yield a reduced absorbance; that Gaussian profile has full width  $\delta\tilde{\nu}$  at half stature. Stature denotes a maximum net reduced absorbance; area denotes an integral of reduced absorbance over a particular Gaussian feature; both stature and area are only relative values because an absolute amount or thickness of an absorbing sample is unknown.  $\Delta\tilde{\nu}$  indicates the difference between the wavenumber  $\tilde{\nu}$  of a spectral feature and the preceding feature. Values of  $\tilde{\nu}$  within parentheses indicate an upper limit of wavenumber of measurements, and the centre of a Gaussian function to fit absorption remaining up to that limit after other components are fitted. Values of all entries are rounded appropriately to be roughly commensurate with standard errors derived from the fits.

absorption feature but the limit of the spectral scan as imposed by conditions specified below in each case; because strong absorption by some samples persisted at those limits of scans, for which we could fit a Gaussian curve only roughly, those penultimate features in each case are characterized with greater uncertainty than others

**Table 2**

Fitted characteristics of contributions to the spectrum of solid CO<sub>2</sub> (one sequence) and estimated wavenumbers of weak features and their intervals  $\Delta\tilde{\nu}$  in absorption spectra of solid N<sub>2</sub>O (two sequences), both at 10 K<sup>a</sup>

$\tilde{\nu}/\text{cm}^{-1}$	Relative stature/ $10^{-6}$ cm	$\delta\tilde{\nu}/\text{cm}^{-1}$	Relative area	$\Delta\tilde{\nu}/\text{cm}^{-1}$
<b>CO<sub>2</sub></b>				
75 811	0.273	1000	0.000290	
76 438	0.442	695	0.000327	627
76 965	0.704	569	0.000427	527
77 529	1.09	604	0.000703	564
78 146	1.35	623	0.000895	617
78 774	1.44	629	0.000964	628
79 394	1.39	650	0.000958	620
80 036	1.33	724	0.00103	642
80 681	1.07	707	0.000806	645
81 298	0.918	735	0.000718	617
81 887	0.676	716	0.000516	589
82 436	0.555	755	0.000446	549
83 130	0.624	931	0.000620	694
83 754	0.371	600	0.000237	624
<b>N<sub>2</sub>O</b>				
$\tilde{\nu}/\text{cm}^{-1}$				$\Delta\tilde{\nu}/\text{cm}^{-1}$
53 688				1149
54 837				1034
55 871				1110
56 981				1112
58 093				957
59 050				958
60 008				1033
61 041				
64 949				804
65 753				690
66 443				612
67 055				690
67 745				574
68 319				

<sup>a</sup> The notation is the same as for Table 1.

in the same spectrum. Although measurements of wavenumbers are reported in Tables 1 and 2 with multiple digits, their significance is subject to the caveat noted above; all stated uncertainties correspond to one standard error.

### 3. Results

The spectra of the various samples are displayed directly in the accompanying figures; the quantitative results of fitting Gaussian components to the absorbance divided by wavenumber are listed in Tables 1 and 2. Spectra of four samples show evidence of subsidiary structure – for pure NO, pure CO<sub>2</sub>, pure N<sub>2</sub>O and NH<sub>3</sub> dispersed in Ar – whereas other spectra exhibit only broad overlapping lines. We describe the results of analysis separately for each spectrum.

#### 3.1. NO

The curve of pure solid nitrogen oxide in Fig. 1 contains three readily recognisable features, all broad lines. The most prominent feature occurs before the vacuum ultraviolet region, with a maximum near 48 000 cm<sup>-1</sup>; another feature with maximum near 67 000 cm<sup>-1</sup> is much broader but weaker, and a third continuum extends beyond the limit of measurements imposed by the lack of transparency of LiF windows. Four weak features are barely discernible as a weak modulation of the profile of the subsidiary maximum near 67 000 cm<sup>-1</sup>, with centres near wavenumbers/cm<sup>-1</sup> 65 600, 66 800, 68 100 and 69 300 with uncertainties 200 cm<sup>-1</sup>, so with an interval approximately 1200 cm<sup>-1</sup>.

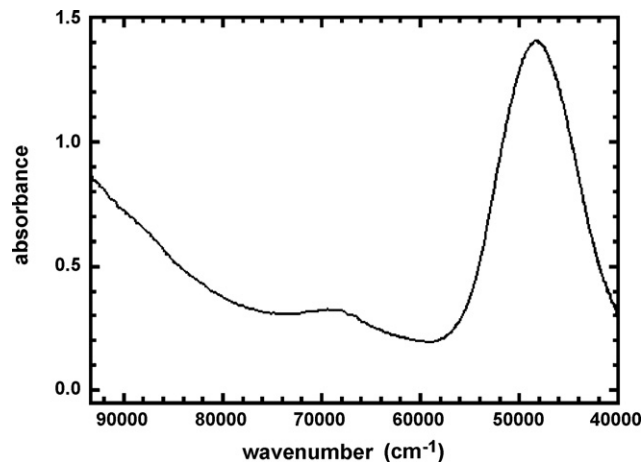


Fig. 1. Absorption spectrum in the vacuum ultraviolet region of solid NO at 10 K; spectral resolution 0.2 nm or 33–174 cm<sup>-1</sup>.

#### 3.2. O<sub>2</sub>

The spectrum of pure solid dioxygen in Fig. 2 contains apparently two broad lines, with maxima near 59 000 and 72 000 cm<sup>-1</sup>, and a hint of a further absorption feature beyond the range of spectral measurement. Fitting the total profile of absorption with three Gaussian contributions, rather than two, yields a significantly improved fit, but otherwise there is no obvious requirement for a broad line centred near 62 000 cm<sup>-1</sup>.

#### 3.3. CO<sub>2</sub>

The spectrum of pure solid carbon dioxide in Fig. 3 contains four distinct regions of features—broad and weak lines with maxima near 54 300 and 70 000 cm<sup>-1</sup>, a region of resolvable fine structure centred about 79 000 cm<sup>-1</sup> and, beyond 84 000 cm<sup>-1</sup>, a much more intense block of absorption of which the shape is atypical of separate electronic or vibrational transitions; the latter region is satisfactorily fitted with three overlapping lines, consistent with the shape of the curve at the top of the block, with the most intense component extending beyond the range of measurement. The characteristics of these six broad features appear in Table 1. The ratio of statures of most intense and least intense fitted components, at either end of the measured spectrum, attains 1000. Between 75 800

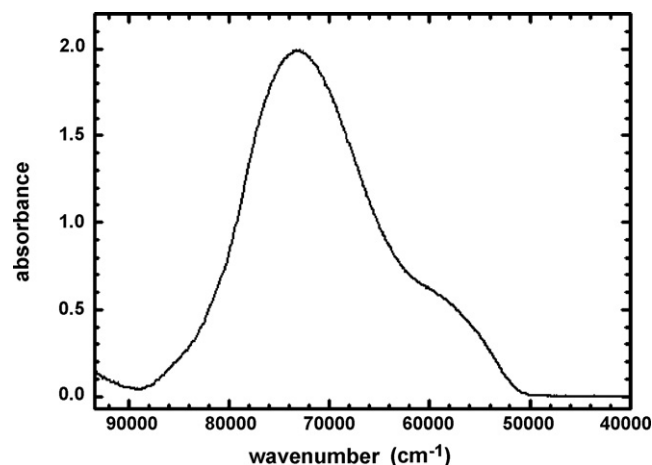
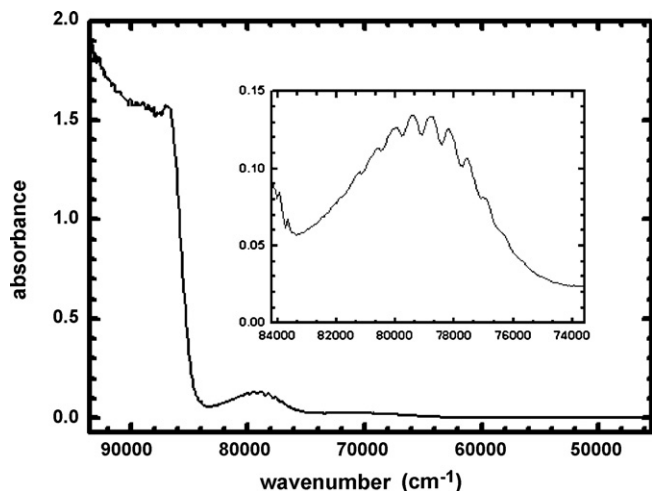


Fig. 2. Absorption spectrum in the vacuum ultraviolet region of solid O<sub>2</sub> at 10 K; spectral resolution 0.2 nm or 33–174 cm<sup>-1</sup>.

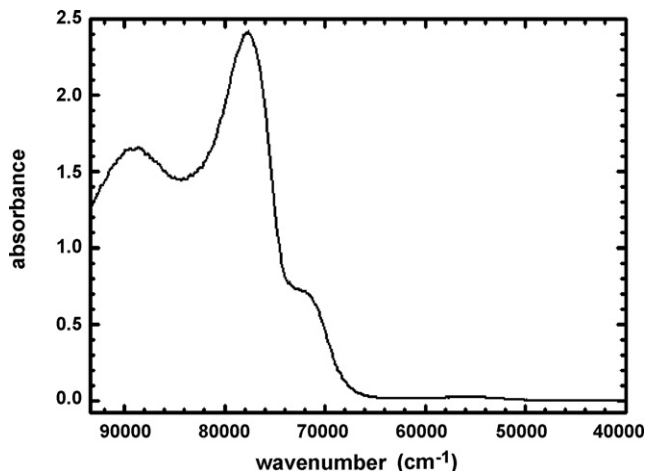


**Fig. 3.** Absorption spectrum in the vacuum ultraviolet region of solid  $\text{CO}_2$  at 10 K: spectral resolution 0.2 nm or  $42\text{--}78\text{ cm}^{-1}$  from 45 000 to 62 500  $\text{cm}^{-1}$ , and 0.1 nm or  $39\text{--}87\text{ cm}^{-1}$  from 62 500 to 95 300  $\text{cm}^{-1}$ ; the inset shows a region near 80 000  $\text{cm}^{-1}$  on an expanded scale.

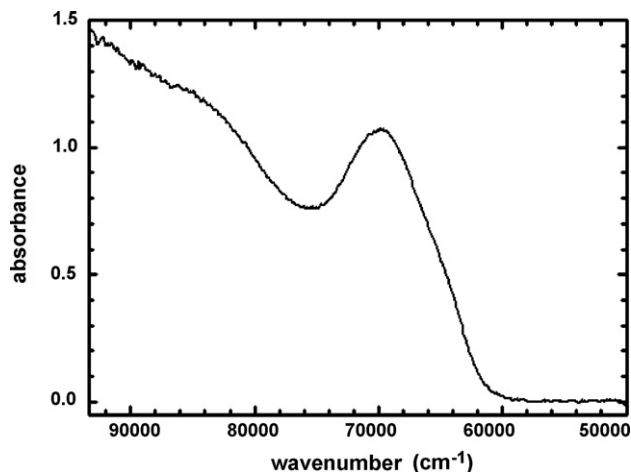
and 83 750  $\text{cm}^{-1}$  as shown in the inset to Fig. 3, the absorption profile is adequately fitted with 14 lines in a sequence, with mean interval  $(611 \pm 42)\text{ cm}^{-1}$  comparable with their fitted widths, of mean  $(710 \pm 190)\text{ cm}^{-1}$ ; the characteristics of these lines are listed in Table 2.

### 3.4. $\text{N}_2\text{O}$

The spectrum in Fig. 4 of solid dinitrogen oxide exhibits only four distinct features, but the fit of the total profile near 65 000 and 79 000  $\text{cm}^{-1}$  seems to require further contributions centred near those locations. The first weak and broad line, with maximum near 55 500  $\text{cm}^{-1}$ , is practically separate from other features, with the other five overlapping lines on either side of the prominent maximum near 77 500  $\text{cm}^{-1}$ . Characteristics of these six features are summarised in Table 1. Close scrutiny of the residual between the total absorption divided by wavenumber and the sum of those six features indicates the presence of two additional series of weak lines, superimposed on much broader and stronger lines; the wavenumbers of their estimated maxima of absorption appear in Table 2. To fit quantitatively these weak lines in the presence



**Fig. 4.** Absorption spectrum in the vacuum ultraviolet region of solid  $\text{N}_2\text{O}$  at 10 K: spectral resolution 0.2 nm or  $33\text{--}174\text{ cm}^{-1}$ .



**Fig. 5.** Absorption spectrum in the vacuum ultraviolet region of solid  $\text{H}_2\text{O}$  at 10 K: spectral resolution 0.2 nm or  $33\text{--}174\text{ cm}^{-1}$ .

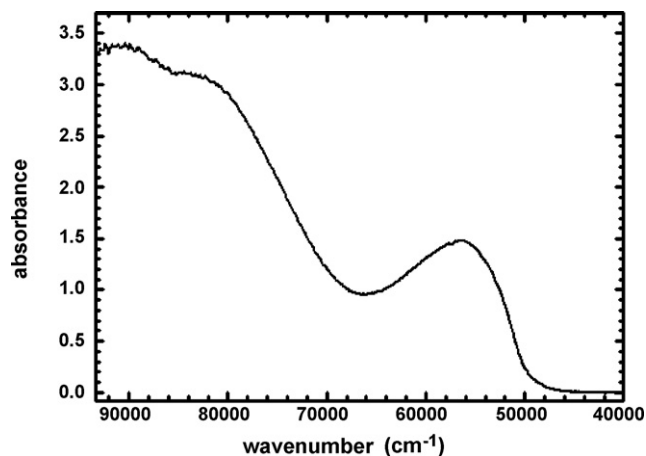
of much more intense and broad features proved impracticable because their statures are at most twice the amplitude of noise, but their widths seem smaller than the separations between adjacent lines. Eight features in the first progression, beginning at 53 688  $\text{cm}^{-1}$  have a mean separation  $(1050 \pm 71)\text{ cm}^{-1}$  between adjacent features, whereas six features in a second progression, beginning at 64 949  $\text{cm}^{-1}$ , have a mean separation  $(674 \pm 79)\text{ cm}^{-1}$ . In neither case is there a significant indication of a systematic variation of separations along the sequences.

### 3.5. $\text{H}_2\text{O}$

As is evident from visual inspection of Fig. 5, the absorption spectrum of solid  $\text{H}_2\text{O}$  at 10 K, likely an amorphous glass rather than crystalline ice, requires only four contributions to fit the total profile—a true maximum near 69 000  $\text{cm}^{-1}$ , its masked shoulder near 65 000  $\text{cm}^{-1}$ , a broader maximum near 86 000  $\text{cm}^{-1}$  and a further feature extending beyond the range of measurement.

### 3.6. $\text{NH}_3$ pure

For pure solid ammonia the broad maximum in Fig. 6 near 56 000  $\text{cm}^{-1}$  requires three contributions for a satisfactory account of the absorption; another maximum near 82 000  $\text{cm}^{-1}$  and a fur-



**Fig. 6.** Absorption spectrum in the vacuum ultraviolet region of solid  $\text{NH}_3$  at 10 K: spectral resolution 0.2 nm or  $33\text{--}174\text{ cm}^{-1}$ .



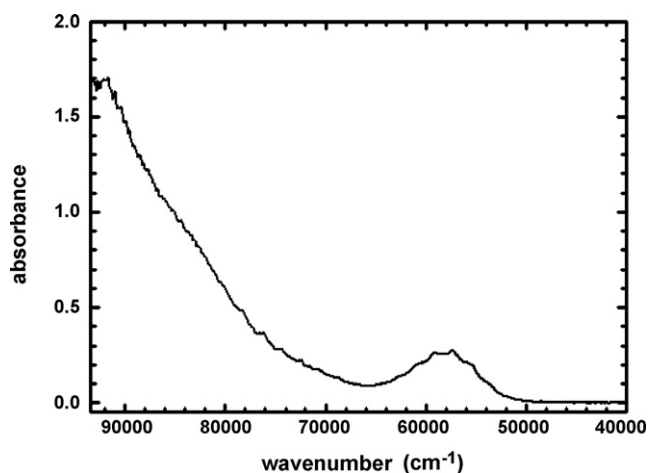


Fig. 7. Absorption spectrum in the vacuum ultraviolet region of  $\text{NH}_3$  dispersed in solid Ar (molar ratio 250) at 10 K: spectral resolution 0.1 nm or  $16\text{--}51\text{ cm}^{-1}$  from 40 000 to 71 500  $\text{cm}^{-1}$  and 0.2 nm or  $102\text{--}174\text{ cm}^{-1}$  from 71 500 to 95 200  $\text{cm}^{-1}$ .

ther feature extending beyond the range of measurement complete a quantitative rendering of this spectrum.

### 3.7. $\text{NH}_3$ dispersed in Ar

This spectrum in Fig. 7 contains two major regions of absorption, with maxima near 57 000 and 92 000  $\text{cm}^{-1}$ , but the former exhibits distinct evidence of structure; the progressive differences between consecutive members of these sets appear in the fifth column of Table 1. In this sequence seven lines, after that at 52 518  $\text{cm}^{-1}$  that is much broader than succeeding lines, have a mean interval  $(1800 \pm 60)\text{ cm}^{-1}$ , comparable with their mean widths  $(1920 \pm 180)\text{ cm}^{-1}$ . Although a further sequence is not directly obvious from the total profile of absorption, the residual absorption, after subtraction of the former sequence and broad lines centred near 88 000  $\text{cm}^{-1}$  and approaching the limit of measurements from the total absorption, definitely indicates seven additional weak lines superimposed on the specified background; according to that list in Table 1, the mean interval  $(1900 \pm 120)\text{ cm}^{-1}$  is perceptibly larger than the mean of the preceding sequence, and the line widths decrease slightly with increasing wavenumber of their position.

## 4. Discussion

All spectral absorption in this vacuum ultraviolet region pertains directly to electronic transitions, which might be accompanied by vibrational structure. In contrast with gaseous samples under conditions in which the mean free path of molecules is much greater than molecular dimensions and the duration of an absorption event is much smaller than the interval between collisions, in a solid sample an overlapping of electronic density occurs between adjacent molecules; a transition dipole in one molecule can resonate with those in adjacent molecules of the same type or even in other atomic or molecular species that have transitions possible at comparable energies. For a sample of a pure solid element or compound, an attribution of a particular absorption feature to an electronic transition within a particular single molecule is questionable, but a collective transition of the entire sample, or crystallite thereof, is equally unlikely for energies sufficient to excite low-lying electronic states of an individual molecule. Even at the latter energies of excitation, the delocalised or expanded nature of a particular molecule in an excited electronic state, which might invade the space of at least a few molecules adjacent to one in which a par-

ticular absorption event might be supposed to occur, blurs the identity of a particular absorbing molecule, and produces features in the absorption spectrum that have widths much greater than those of transitions in the same spectral region characteristic of free molecules in the gaseous phase. The width of an apparent feature in a spectrum of a solid compound is thus generally greater than the width of a corresponding feature in spectra of that same compound dispersed in solid argon. Under the conditions of our samples, evidence for rotational structure of any molecule is lacking, even for restricted rotation; in any case the widths of features and their separations are hundreds of times the magnitude of the rotational parameters of individual molecules, but those widths and separations might be comparable with wavenumbers associated with intramolecular vibrational modes.

The samples on which we undertook spectral measurements for this project comprise two diatomic oxides – NO and  $\text{O}_2$ , two linear triatomic oxides –  $\text{CO}_2$  and  $\text{N}_2\text{O}$ , and two angular polyatomic hydrides –  $\text{H}_2\text{O}$  and  $\text{NH}_3$ , the latter compound as both a neat solid film and dispersed in solid argon. To emphasize the similarities and differences between spectra of comparable species, we discuss these spectra according to these couples.

### 4.1. $\text{O}_2$ and NO

Whereas in the vacuum ultraviolet region gaseous  $\text{O}_2$  has a sparse pattern of molecular energies corresponding to purely electronic transitions but much accompanying vibrational and rotational structure, NO has several electronic systems [1,3]. The prominent system B–X of gaseous  $\text{O}_2$  that begins in the near ultraviolet and becomes progressively more intense before the onset of a continuum beyond 60 000  $\text{cm}^{-1}$  would seem to correspond to the first broad component in our spectrum, which lacks any vestige of the abundant vibrational (and rotational) structure so evident in the gaseous spectrum. For the second and even more intense absorption feature of solid  $\text{O}_2$  there seems to exist no directly corresponding transition of single  $\text{O}_2$  molecules. Alternatively, the first broad line might correspond to the forbidden transition A–X, enhanced through intermolecular interactions, and the second broad line to the more intense transition to B–X, but such assignments would entail much larger blue shifts from gaseous to solid phases.

For solid NO the intense but structureless line with maximum absorption near 48 000  $\text{cm}^{-1}$  doubtless corresponds to the system B–X of the free molecule. The fitted Gaussian curve for this absorption line of solid NO notably underestimates the measured absorption near 40 000  $\text{cm}^{-1}$ ; the difference likely reflects some absorption into the system A–X that is also observable in the spectrum of a gaseous sample. The other systems C, D, E–X for gaseous NO all have Rydberg character; their apparent absence from the spectrum of solid NO is consistent with the observation that transitions to electronic states with Rydberg character are, in condensed phases, either altered to much greater energies or otherwise suppressed [16], consistent with direct observations for NO dispersed in solid Ar [17]. For the broad line of solid NO with maximum near 67 000  $\text{cm}^{-1}$ , no assignment is proffered; the weak structure superimposed on this broad line has, between the three members, an interval about 1200  $\text{cm}^{-1}$ ; this value resembles the vibrational spacing, about 1030  $\text{cm}^{-1}$ , in state B near 48 000  $\text{cm}^{-1}$  in the absorption spectrum of gaseous NO [1,3]. The more intense absorption extending beyond our range of measurement likely includes contributions from transitions of NO molecules into states C, D and E.

In cases of both solid NO and solid  $\text{O}_2$ , the absence of vibrational structure contrasts strongly with our measurements of the spectrum of solid CO [4] in which a well developed progression

of vibrational lines is evident, although, like NO and O<sub>2</sub>, any vibrational features at greater transition energies are entirely diffuse. For both NO and O<sub>2</sub>, the nature of the absorption profiles in the ultraviolet region differs significantly between spectra of gaseous and solid samples. Although CO has abundant features in this vacuum ultraviolet region 110–200 nm in absorption in both gaseous and solid phases [4], it is remarkable that O<sub>2</sub> with two additional electrons that has electronic transitions in the near infrared and visible regions [18] has such sparse content in its spectra in the solid phase.

#### 4.2. CO<sub>2</sub> and N<sub>2</sub>O

The weak modulation of the profile of the feature about 79 000 cm<sup>-1</sup> of solid CO<sub>2</sub> comprises a progression with 14 discernible members; the mean vibrational interval 611 cm<sup>-1</sup> is similar to the wavenumber associated with the vibrational mode in the electronic ground state due to angular deformation. The length of this progression and its vibrational interval strongly imply a transition from a linear electronic ground state to an electronically excited state that is markedly angular. The transition B–X of gaseous CO<sub>2</sub>, in the same region 72 000–82 000 cm<sup>-1</sup> with maximum absorption near 75 000 cm<sup>-1</sup>, is supposed to take the molecule from a linear electronic ground state to just such an angular electronically excited state [19,2], for which the observed vibrational interval is appropriately excited during the transition. Although two further reported progressions of free CO<sub>2</sub> have a wavenumber 1225 cm<sup>-1</sup> attributed to a vibrational mode along the linear molecular axis [20,2], we associate the structured progression in the spectrum of solid CO<sub>2</sub> with an electronic transition B–X; the broad line of solid CO<sub>2</sub> with maximum near 54 000 cm<sup>-1</sup> is likely the counterpart of the absorption of free CO<sub>2</sub> assigned as the transition A–X with maximum near 68 000 cm<sup>-1</sup> in absorption [2]. Monahan and Walker [21] assigned the intense feature near 87 000 cm<sup>-1</sup> with an abrupt onset to an excitonic feature associated with a parallel electronic transition to state C. According to their comparable energies and intensities relative to other features, the remaining two features deduced from the spectrum of solid CO<sub>2</sub> have readily identifiable counterparts in spectra of gaseous CO<sub>2</sub> in intense transitions to states D and E [2] with comparable wavenumbers in both states. This interpretation leaves the broad line with maximum absorption near 70 000 cm<sup>-1</sup> unassigned.

The weak and broad line with maximum near 55 500 cm<sup>-1</sup> of solid N<sub>2</sub>O occurs about the same region as the continuum due to the system A–X of gaseous N<sub>2</sub>O, with maximum near 55 000 cm<sup>-1</sup>. Of the other five deduced features of the spectrum of solid N<sub>2</sub>O, the energies and intensities of the lines with maxima near 72 000, 77 000 and 89 000 likely correspond to transitions of gaseous N<sub>2</sub>O from the electronic ground state to states B with a maximum near 69 000 cm<sup>-1</sup>, C with a maximum near 78 000 cm<sup>-1</sup>, and E and F together near 85 000 cm<sup>-1</sup> [2]. The other two features, near 66 000 and 77 000 cm<sup>-1</sup>, deduced in the spectrum of solid N<sub>2</sub>O seem to have no readily identified counterparts in the spectrum of gaseous N<sub>2</sub>O. Of the two vibrational progressions superimposed on broad continua, the interval of the first is comparable with the wavenumber associated with a parallel vibration of the free molecule in the electronic ground state, whereas the interval of the second is a little larger than the wavenumber associated with angular deformation in the electronic ground state. The presence of a vibrational mode of type angular deformation in a progression indicates strongly an equilibrium structure for the electronically excited state that is angular, unlike the linear conformation of the electronic ground state. For a gaseous sample [22] a sequence of diffuse lines above 58 000 cm<sup>-1</sup> have wavenumber intervals decreasing rapidly from about 800 cm<sup>-1</sup>, just as for the second sequence of N<sub>2</sub>O in Table 2; such a similarity signifies that the electronic transition of N<sub>2</sub>O in

the solid phase is likewise to state B. Monahan and Walker [21] also observed qualitatively such weak vibrational structure, but only four members of the first progression, compared with our eight; that their separations between adjacent features are significantly smaller than our mean separation likely reflects their fewer data. For the second progression the same authors [21] reported six members, of which four are common to our measurements of six members; there is a constant shift ~200 cm<sup>-1</sup> between the common members but the separations within the entire progressions are the same within experimental uncertainties. Roncin and Damany had earlier reported [23,24] a sequence of six lines of pure solid N<sub>2</sub>O between 67 840 and 70 770 cm<sup>-1</sup>; whether these lines are all equivalent to, but merely displaced from by dint of calibration anomaly, those six features that we report between 64 949 and 68 319 cm<sup>-1</sup> in Table 2 is uncertain: we find no evidence in our spectra of a continuation of this sequence beyond 69 000 cm<sup>-1</sup>. For both N<sub>2</sub>O and CO<sub>2</sub>, there are thus similarities between spectra of gaseous and solid samples, although some features of the latter spectra remain unexplained quantitatively.

#### 4.3. H<sub>2</sub>O and NH<sub>3</sub>

The two most prominent features of the spectrum of solid H<sub>2</sub>O, with maxima near 69 000 and 85 000 cm<sup>-1</sup> correlate readily with diffuse absorption systems of gaseous H<sub>2</sub>O with maxima near 60 000 and 79 000 cm<sup>-1</sup> assigned to transitions A–X and B–X, respectively, with an appreciable blue shift in either case. Even the shoulder feature deduced in the curve of solid H<sub>2</sub>O might have its counterpart in the spectrum of the gaseous sample, as there is, in the latter, diffuse structure for which simplification might occur on solidification of H<sub>2</sub>O. For a further intense absorption toward the limit of our observations on solid H<sub>2</sub>O there are electronic states of free H<sub>2</sub>O to which transitions are known in the same region. Our spectrum is measured over a greater domain of wavenumber than those of Dressler and Schnepf [4] and of Chergui and Schwentner [25], and appears to be of superior quality. The important conclusion [4] of a large shift to greater energy of the onset of absorption in the solid phase, relative to the gaseous phase, is confirmed, for both H<sub>2</sub>O and NH<sub>3</sub>. Chergui and Schwentner [25] made their analysis on an interpretation in terms of orbitals; as orbitals are artefacts of a wave-mechanical calculation and have no physical existence [26], that interpretation is at best speculative. Perhaps the inferior quality of that spectrum and the lack of a quantitative fitting technique prevented these authors from discovering the essential contribution of an absorption feature near 64 600 cm<sup>-1</sup> to the total absorption in this region.

Like solid H<sub>2</sub>O, solid NH<sub>3</sub> yields a spectrum of broad lines, but a complication absent for other species investigated here is the fact that the wavenumber 81 900 cm<sup>-1</sup> corresponding to the first ionization energy of NH<sub>3</sub> lies well within our range of spectral observation. Purely on a basis of these diffuse spectra, one can in no way identify whether ionization plays a part in contributing to the observed spectral features. Qualitative comparison is, however, practicable between the spectrum of gaseous NH<sub>3</sub>, which contains three regions of bands in vibrational progressions and a further continuum, and solid NH<sub>3</sub>, of which the four deduced features, beyond the first feature that appears within the shoulder of the line exhibiting a local maximum of absorption, are listed. On this basis, the weak second system of gaseous NH<sub>3</sub> might be present in the region of the minimum of absorption of solid NH<sub>3</sub>, in which region the absorption is still appreciable.

In contrast to the entirely diffuse spectra of neat solid H<sub>2</sub>O and of neat solid NH<sub>3</sub>, two progressions of diffuse structure appear for NH<sub>3</sub> dispersed in solid Ar. The first progression shows intervals near 1800 cm<sup>-1</sup> for the sequence of seven members with the first at

53 740  $\text{cm}^{-1}$ , continuing over the maximum about 57 000 to about 66 000  $\text{cm}^{-1}$ ; the second progression with larger intervals surmounts the rising background about 74 000  $\text{cm}^{-1}$ . These intervals are approximately twice the intervals 950  $\text{cm}^{-1}$  associated with a progression of gaseous  $\text{NH}_3$  having maximum absorption near 52 000, and 1000  $\text{cm}^{-1}$  with another progression having maximum absorption near 65 000  $\text{cm}^{-1}$  [2]; the electronically excited states A and B reached through these transitions have planar equilibrium structures [2]. In both cases an appreciable blue shift seems evident in the spectra of  $\text{NH}_3$  dispersed in Ar relative to gaseous  $\text{NH}_3$ . The nature of diffuse structure with maxima deduced near 88 000  $\text{cm}^{-1}$  and beyond the range of measurement is unknown; whether ionization is involved here is likewise undecipherable. Apart from the more pronounced nature of the absorption near 80 000  $\text{cm}^{-1}$ , and the more diffuse features of the spectrum of solid  $\text{NH}_3$ , the general shapes of the profiles for both pure  $\text{NH}_3$  and  $\text{NH}_3$  dispersed in Ar are similar; this condition tends to indicate that in either case the transitions are primarily intramolecular, rather than involving multiple  $\text{NH}_3$  molecules that is feasible in neat solid ammonia.

Dressler [7] reported a vacuum ultraviolet spectrum, in a domain 150–190 nm, of both an allegedly pure film of ammonia and dispersions of  $\text{NH}_3$  in argon at molar ratios 10, 33, 100 and 330, all at 4 K. The only feature of the absorption of neat solid ammonia was a single narrow line at 194 nm (51 550  $\text{cm}^{-1}$ ) of estimated width 2.5 nm (660  $\text{cm}^{-1}$ ). Our spectra show no trace of the latter feature, which might have arisen from some photodecomposition of that sample during its simultaneous exposure to all wave lengths within the stated range, to which Dressler alluded [7]; our samples were exposed to only radiation pre-dispersed by a monochromator to a particular wave length, which minimizes not only photolysis of the sample during spectral measurements but also any heating or annealing effect on the sample.

For a sample of  $\text{NH}_3$  in Ar at a molar ratio 100 recorded with a spectrograph, Dressler [7] noted also five weak and broad features at wave length/nm (wavenumber/ $\text{cm}^{-1}$ ) 186.7 (53 562), 180.6 (55 371), 174.9 (57 176), 169.2 (59 102) and 164.0 (60 976); these wavenumbers exhibit a progressive systematic difference decreasing from +177 to –151  $\text{cm}^{-1}$  from our corresponding measurements, listed in Table 1, based on a spectrum of much greater quality, but the trend of a sequence of weak features of comparable intervals is common to measurements in both sets. On the basis of infrared absorption lines of  $\text{NH}_3$  in solid Ar and solid  $\text{N}_2$  a phenomenon of molecular rotation was inferred [27] to occur in both cases; among inconsistencies of such an interpretation are that lines are assigned in branch R for which the corresponding lines in branch P are absent, and that the inversion splitting of mode  $\nu_2$  decreased markedly from 35.58  $\text{cm}^{-1}$  for free  $\text{NH}_3$  to 18  $\text{cm}^{-1}$  purportedly for  $\text{NH}_3$  in  $\text{N}_2$  and to only 8  $\text{cm}^{-1}$  for  $\text{NH}_3$  in Ar [27]. An explanation of our vacuum ultraviolet spectra on such a basis of freely rotating molecules hence seems unwarranted. We regard the intervals 1800 and 1900  $\text{cm}^{-1}$  in our spectra as instead implying twice the wavenumber of a vibrational mode  $\nu_2$  in pyramidal  $\text{NH}_3$  in its electronic ground state that takes the molecule to a planar equilibrium structure in the two electronically excited states reached as the results of transitions with wavenumbers near 57 000 and beyond 75 000  $\text{cm}^{-1}$ , consistent with careful analysis of spectra of gaseous samples [28–31].

## 5. Conclusion

For samples of six molecular species, one elemental and five compounds, either pure or, for ammonia, also dispersed in solid

argon, all at 10 K, we report here new measurements of their absorption spectra in the vacuum ultraviolet region, upon which we have undertaken a quantitative reduction to distinguish contributions to the total absorption of Gaussian profiles. By comparison with previously measured spectra of gaseous samples, we suggest some assignments based on both energies and intensities, but the nature of these solid samples makes definitive assignments impractical. Despite this ambiguity, the measurement of spectra, in the vacuum ultraviolet region, of small molecules in both gaseous and condensed phases is important in relation to the understanding of both photochemical processes and interactions between excited molecules and either other molecules of the same species or other, simple atomic, species in close proximity. The similarity between our spectra of ammonia pure and dispersed in argon contrasts with the spectra of other compounds under these conditions.

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