Absorption spectra in the vacuum ultraviolet region of methanol in condensed phases

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Abstract

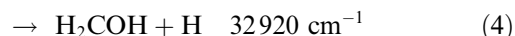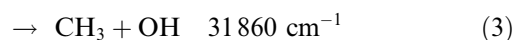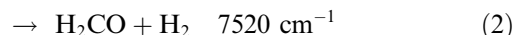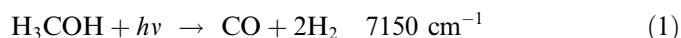With radiation from a synchrotron we measured the spectra of pure solid methanol and of methanol dispersed in solid argon (molar ratio 200) and krypton (molar ratio 250) at 10 K from the onset of absorption in the vacuum ultraviolet region until the limits imposed by LiF windows or the Ar or Kr dispersant. 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 methanol and with energies and intensities from our published quantum-chemical calculations.
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1. Introduction

Numerous investigations of photoreactions of methanol (H_3COH) have been reported because of its importance in planetary atmospheres [1–4]. The thresholds for photodissociation of OH from H_3COH in solid Ne and Ar were determined from fluorescence spectra [5]. We measured the cross sections for absorption and the rates of solar photodissociation of gaseous methanol in deuterated variants, and performed extensive calculations on low-lying excited states of methanol using a basis set designated TD-DFT/cc-pV5Z [6,7]. The photoexcitation of methanol in condensed phases, however, remains poorly understood.

According to standard thermodynamic data, here are the wavenumbers of thresholds for possible photodissociative reactions of free methanol.

$$H_3COH + h\nu \rightarrow CO + 2H_2 \quad 7150 \text{ cm}^{-1} \quad (1)$$
$$\rightarrow H_2CO + H_2 \quad 7520 \text{ cm}^{-1} \quad (2)$$
$$\rightarrow CH_3 + OH \quad 31860 \text{ cm}^{-1} \quad (3)$$
$$\rightarrow H_2COH + H \quad 32920 \text{ cm}^{-1} \quad (4)$$
$$\rightarrow H_3CO + H \quad 35650 \text{ cm}^{-1} \quad (5)$$
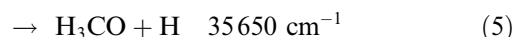
All continua in the spectrum of gaseous methanol [6], shown in Fig. 1 with an abscissal scale linear in wavenumber, appear at much greater energies or wavenumbers than these listed values. Moreover, the photochemical properties of confined molecules in a condensed phase differs from that of free molecules in the gaseous phase because a molecular fragment resulting from dissociation encounters hindrance to escape from its original site within its site of production; for that reason a much increased photonic energy might be required to produce a free radical stabilised sufficiently remotely from a partner product with which it might recombine. For instance, we probed the fluorescent signal of OH produced through reaction (3), but the yield of H_3CO or H_2CO in a Ne or Ar matrix was small [5]; the threshold energy required to make such

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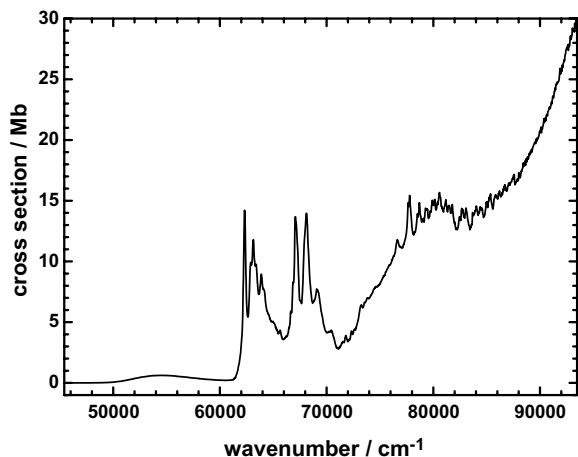
Fig. 1. Absorption cross section of methanol vapour in the vacuum ultraviolet region, replotted from Ref. [6]; spectral resolution 0.05 nm or ~30 cm^{-1}.

a stabilized OH radical in Ar detectable corresponds to a wavenumber $(57\,140 \pm 330)$ cm^{-1}, which is not only appreciably greater than the onset of absorption that we have measured in the present work but even almost twice the wavenumber stated for reaction (3) above. A study of absorption spectra of methanol in condensed phases can clearly provide information about possible thresholds for its photochemical decomposition in varied environments into various products.

Experiments on the photodissociation of H_2O in solid Ne, Ar, Kr and Xe demonstrated that the threshold energies for the production of OH are greater than those in the gaseous phase [8–10], are identical to the thresholds of absorption of H_2O in Ne, Ar and Kr, but are 0.2 eV less than the threshold energy of absorption of H_2O in Xe [11]. Zoval and Apkarian found that the thresholds of absorption of H_2S in solid matrices correspond to ~1.7 eV excess energies of dissociation [12]. These photolytic reactions involve breaking an O–H or S–H bond to produce atomic H. With a hydrogen atom in water becoming replaced with a methyl group, methanol exhibits spectral features similar to, but distinct from, those of water. Because of the multiple channels presented above, the photodissociation of methanol is much more complicated than for water in the condensed phase. The absorption spectra of H_3COH in condensed phases hence warrant investigation to acquire information pertinent to photodissociation. We have measured the absorption spectra of methanol as a neat solid film and dispersed in solid argon and krypton; we present here our analysis of those spectra. Like the analysis of spectra of gaseous compounds such as methanol [6], the gleaning of quantitative data from spectra in condensed phases that include both narrow and broad contributions that are poorly resolved remains a considerable challenge; we demonstrate here how we have deduced semiquantitative knowledge of electronic and vibrational structure from such spectra.

2. Experiments and analysis of data

We measured absorption spectra in the vacuum ultraviolet region of condensed and gaseous samples with a double-beam absorption apparatus, described previously [13]. 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 lengths were calibrated with absorption lines of Xe [14], CO [15,16], O_2 [17], and NO [18–21]. A small fraction of the light beam was reflected from a LiF crystal plate placed at an angle 45° to the beam line before the gas cell or 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, constant on a wave length scale, is specified with each figure.

For measurements on a sample in a condensed phase, a cryostat replaced the gas cell. 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 impinged onto a window (glass, coated with sodium salicylate) from which the converted visible light was measured with another photomultiplier. The gaseous mixtures were prepared according to standard manometric procedures in an ultra-high vacuum system designed for that purpose. The rate of deposition was regulated in a range/nmol s^{-1} [7.4, 220], as monitored with a flow transducer. The duration/s of deposition was typically 180–1800. For absorption by a gas, the light transmitted through the beam splitter (LiF) passed a cell containing the sample equipped with two end windows (LiF), and impinged onto a window (glass, coated with sodium salicylate); the length of optical path within the gas cell is 0.0847 m. The density of the gas was determined from the pressure recorded with a capacitance manometer (MKS, Baratron) and the temperature was monitored with a thermocouple.

Argon Ar (Matheson, nominal purity 99.9999%) and krypton Kr (Matheson, nominal purity 99.999%) were used directly without further purification. Methanol (H_3COH in natural abundance, Merck, spectroscopic grade, nominal purity 99.999%) was degassed at 77 K three times; the degassed sample was subsequently purified further by vacuum distillation from 195 to 77 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 pure solid argon or krypton, and finally a spectrum of pure solid methanol, or methanol dispersed in argon, or methanol dispersed in krypton. From a ratio of the latter spectrum of dispersed methanol with the spectrum for pure argon or krypton as

diluent we subtracted the spectrum of the background; for pure solid methanol we merely subtracted the 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 and, to eliminate the frequency factor from absorption intensity, divided the absorbance by the wavenumber at each point to generate a curve that we fitted with gaussian profiles. Numerical characterization of each gaussian curve in a form of the wavenumber of their centre, relative stature (reduced net absorbance), full width at half the stature and relative area appears in Table 1 for the three conditions of pure solid methanol and methanol dispersed in solid argon and krypton. The width of the features, not the spectral resolution, limits the precision of those measurements; the uncertainty of the central wave-

numbers, as indicated from reproducibility, is likely about 10% of the width in each case. The wavenumbers enclosed within parentheses signify not the maximum of an absorption feature but the limit of the spectral scan as imposed by conditions specified below in each case; because strong absorption by the sample persisted at those limits of scans, for which we could fit a gaussian curve only roughly, the penultimate features in each case are characterized with greater uncertainty than others in the same spectrum. Although measurements of wavenumbers are reported in Table 1 with multiple non-zero digits, their significance is subject to the caveat noted above.

3. Results

The spectrum of neat solid H_3COH at 10 K is shown with normalized absorbance in Fig. 2 in the spectral region 45 000–93 500 cm^{-1}; for comparison, the absolute cross-section of absorption of gaseous CH_3OH at 300 K is plotted in Fig. 1 [6]. In pertinent portions of this vacuum ultraviolet region, absorption spectra of methanol dispersed in a solid noble gas at molar ratios $H_3COH/Ar = 1/200$ and $H_3COH/Kr = 1/250$ at 10 K are displayed in Figs. 3 and 4, respectively.

3.1. Neat solid H_3COH

According to Fig. 2, the absorption of pure solid H_3COH at 10 K exhibits in this vacuum ultraviolet region no distinct local maximum. This absorption begins from its threshold at a wavenumber $(53\,760 \pm 120)$ cm^{-1}, corresponding to energy (6.666 ± 0.015) eV, and increases monotonically to the limit of our observations, but discernible points of inflexion indicate the presence of overlapping broad features. Fitting of the absorption profile normalized by division of wavenumber with two gaussian forms

Table 1
Characteristics of fitted gaussian profiles in spectra of methanol H_3COH as a pure solid and dispersed in solid argon and krypton at 10 K[a]

$\tilde{v}$/cm^{-1}	Relative stature/10^{-6} cm	$\delta\tilde{v}$/cm^{-1}	Relative area/10^{-1}
Neat methanol			
68 180	3.3	9800	0.35
84 730	13.2	23 700	2.7
(94 220)	13.3	8300	0.52
Methanol/200 argon			
54 330	0.82	3170	0.028
58 730	1.1	3350	0.040
63 930	2.1	7350	0.16
68 820	6.0	2310	0.15
70 940	2.9	3550	0.11
73 460	3.4	1080	0.041
74 370	3.4	580	0.021
75 170	1.5	1090	0.017
87 070	25.0	21 300	3.8
(91 030)	13.5	4900	0.36
Methanol/250 krypton			
60 140	0.21	7700	0.17
66 350	0.77	750	0.062
66 480	0.53	5500	0.31
67 240	0.76	920	0.073
68 320	0.77	1350	0.11
69 460	0.80	1050	0.089
70 250	1.3	820	0.12
71 140	1.6	890	0.15
71 760	0.39	540	0.022
72 340	1.5	1190	0.19
73 480	1.4	1350	0.20
74 650	0.80	1400	0.12
(76 410)	3.1	4000	0.70

[a] $\tilde{v}$ denotes a centre of a gaussian profile fitted to a curve of measured absorbance divided by wavenumber/cm^{-1} to yield a reduced absorbance; that gaussian profile has full width $\delta\tilde{v}$ at half maximum stature. Stature denotes a maximum net absorbance, and 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. Values of $\tilde{v}$ 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 have been rounded appropriately to be roughly commensurate with standard errors derived from the fits.
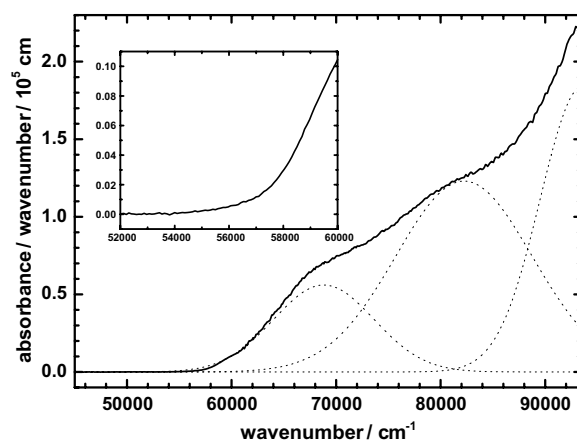

Fig. 2. Absorption in the vacuum ultraviolet region of neat solid methanol at 10 K: the ordinate of points on the full curve is the measured absorbance divided by wavenumber; the dashed lines indicate fitted contributions of gaussian shape; on an expanded scale the inset shows the onset of absorption near 54 000 cm^{-1}; spectral resolution 0.25 nm or ~90 cm^{-1}.

Fig. 3. Absorption in the vacuum ultraviolet region of methanol dispersed in solid argon (molar ratio 200) at 10 K: the ordinate of points on the full curve is the measured absorbance divided by wavenumber; the dashed lines indicate fitted contributions of gaussian shape; on an expanded scale the inset shows the onset of absorption near 51 500 cm^{-1}; spectral resolution 0.2 nm or ~75 cm^{-1}.
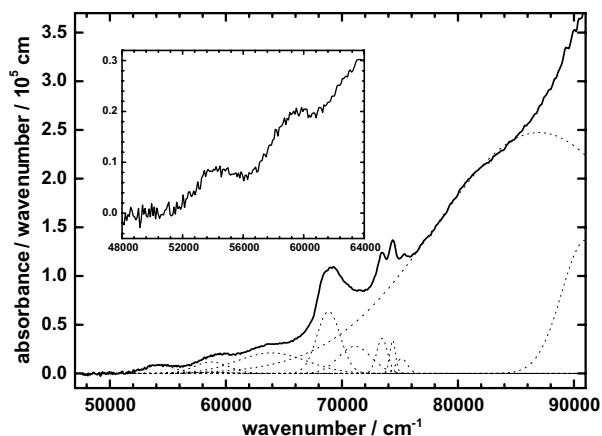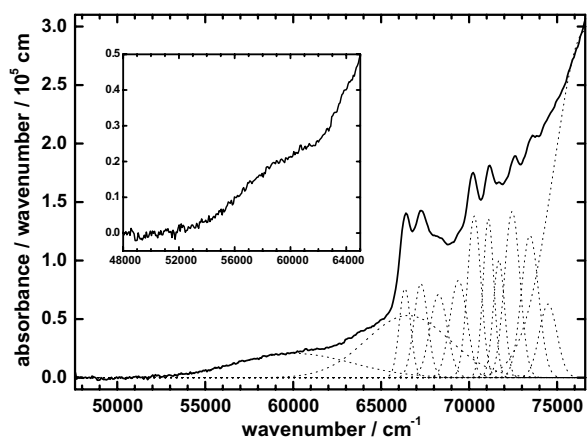

Fig. 4. Absorption in the vacuum ultraviolet region of methanol dispersed in solid krypton (molar ratio 250) at 10 K: the ordinate of points on the full curve is the measured absorbance divided by wavenumber; the dashed lines indicate fitted contributions of gaussian shape; on an expanded scale the inset shows the onset of absorption near 51 500 cm^{-1}; spectral resolution 0.2 nm or ~75 cm^{-1}.

yielded maxima of those forms near 68 000 cm^{-1} with a full width 10 000 cm^{-1} at half maximum and near 85 000 cm^{-1} with width 24 000 cm^{-1}; the ratio of their areas is 1:8 in the same order; the energies corresponding to those fitted maxima are 8.45 and 10.5 eV. That fit indicated a further and much more intense absorption with a maximum beyond the range of observation that was limited by the transmission of LiF crystals to energies less than ≈11.6 eV. The results of fits to all spectra in condensed phases appear in Table 1.

3.2. H$_3$COH dispersed in solid Ar

In a region/cm^{-1} [48 000–64 000], Fig. 3 (inset) shows three weak broad features beyond the threshold of absorp-

tion, near (51 440 ± 90) cm^{-1} or energy (6.378 ± 0.011) eV. Fitting the normalized curve of absorption yielded one maximum near 54 300 cm^{-1} with width 3200 cm^{-1}, a second maximum near 59 000 cm^{-1} with width 3400 cm^{-1}, and a third near 64 000 cm^{-1} with width 7000 cm^{-1}; their areas have a ratio 1:1.5:6. Beyond these diffuse absorptions, prominent local maxima appear. The first of these, near 69 000 cm^{-1} with width 2300 cm^{-1}, is much broader than the succeeding three deduced components, with maxima at 73 460, 74 370 and 75 170 cm^{-1} and widths about 1000 cm^{-1}; the latter three features resemble collectively a short vibrational progression, and their combined areas are about 0.53 times the area of the preceding and broader line. For a broad feature centred near 71 000 cm^{-1} there is scant direct evidence from inspection of the profile of absorption, but an adequate fit of the total absorption in this region requires its presence. Between two inflexion points a broad and intense diffuse feature appears to be associated with a maximum near 87 000 cm^{-1} and width 21 000 cm^{-1}, before a further major absorption with a maximum beyond the limit of observation. With these ten features, of which the last is necessarily poorly defined, we account nearly quantitatively for the recorded absorption of methanol dispersed in solid argon in the vacuum ultraviolet region.

3.3. H$_3$COH dispersed in solid Kr

In the range of observations in Fig. 3 up to ≈9.5 eV, from the apparent onset of absorption of methanol guest near (51 800 ± 100) cm^{-1} or (6.424 ± 0.012) eV until the limit of observation precluded by krypton in great excess, there are several features that we interpret as lines superimposed on three broad features. Of the latter, the first with maximum near 60 000 cm^{-1} has a fitted width near 8000 cm^{-1} whereas the maximum of the third is beyond the range of measurement; the other broad feature, with a fitted maximum near 66 500 cm^{-1} and width 5500 cm^{-1}, is not prominent in the figure, but its presence, indicated by points of inflexion, is required to account satisfactorily for the total absorption attributed to methanol guest; the ratio of the areas of these three features is approximately 1:2:>4. Of the narrow features, there seem to be two progressions. The origin of the first such progression, comprising four members with intervals about 1000 cm^{-1} (average), appears to be about 66 400 cm^{-1}. The next six narrow features indicate a second progression numbering five components within a range from 70 300 to 74 700 cm^{-1}, thus with a mean separation about 1100 cm^{-1}; a further narrow feature near 71 800 cm^{-1} seems required to yield an adequate fit but clearly does not belong to that progression. The diffuseness of this pattern of absorption greatly hinders an accurate fit of the component features, but no component is included in this fit without a direct indication, through either a true local maximum of absorption or an unambiguous point of inflexion, of its participation in the total absorption.

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 overlapping of electronic density occurs between adjacent molecules, and 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 pure solid methanol, 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 electronically excited state, which might invade the space of at least a few molecules adjacent to one in which a particular 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 characteristic of free molecules in the gaseous phase, as exhibited in Fig. 1. The width of an apparent feature in the spectrum of solid methanol is thus greater than the width of almost any feature deduced in spectra of methanol dispersed in argon or krypton. Under the conditions of our samples, evidence for rotational structure of methanol is lacking, even for restricted or internal rotation; in any case the widths of features and their separations are hundreds of times the magnitude of the rotational parameters of individual methanol molecules, but those widths and separations are comparable with wavenumbers associated with intramolecular vibrational modes. Our spectra of gaseous and solid methanol and of methanol dispersed in argon transcend the minimum energy, 10.85 eV, equivalent to $87\,500\,\mathrm{cm}^{-1}$, required to ionize a free molecule [22].

Comparison of calculated wavenumbers and oscillator strengths for free methanol [6] with our present data for solid methanol indicates that the likely correlations are a transition $2\,^1A'' \leftarrow X\,^1A'$ with the first diffuse feature about $68\,000\,\mathrm{cm}^{-1}$ and a transition $3\,^1A' \leftarrow X\,^1A'$ for the second diffuse feature about $85\,000\,\mathrm{cm}^{-1}$, for which the relative intensities are appropriate; alternatively the first diffuse feature might correlate with transitions to both states 2 and 3 and the second diffuse feature to both states 4 and 5 [6]. For a further diffuse feature with maximum absorption somewhere beyond $93\,000\,\mathrm{cm}^{-1}$, an ionization might contribute with other transitions within a neutral molecule for which calculated intensities are not given [6]. For the first electronic transition discernible in spectra of gaseous

methanol, in the region $45\,000–60\,000\,\mathrm{cm}^{-1}$, either the equivalent transition in solid methanol is too weak to be detected under our conditions of samples or the transition might have shifted to greater energy [23] so as to underlie other observed absorption features.

For methanol dispersed in solid krypton, the first broad feature with its maximum near $60\,000\,\mathrm{cm}^{-1}$ likely correlates satisfactorily with a transition to excited state $1\,^1A''$, according to calculations for free methanol [6]; a moderate shift to greater wavenumber, here, is typical of a solid sample relative to the corresponding gaseous sample. The two series of apparent vibrational progressions would seem to correlate with the corresponding progressions associated with transitions to two electronic states $2\,^1A''$ and $3\,^1A''$ or $3\,^1A'$; their relative integrated intensities are roughly comparable with both the calculated and observed oscillator strengths for gaseous methanol [6]. For the most intense absorption at the limit of observations, an assignment to a transition to $4\,^1A''$ or $4\,^1A'$ would likewise correlate with the corresponding transition of gaseous methanol. Because that limit near $77\,000\,\mathrm{cm}^{-1}$ for methanol in krypton corresponds to the onset of absorption by krypton itself, a strong interaction between an excited molecule of methanol and adjacent host atoms of noble gas is possible, which would preclude an assignment to an isolated guest molecule.

Within the first four narrow components of the absorption of methanol dispersed in solid krypton, from $66\,350$ to $69\,460\,\mathrm{cm}^{-1}$, the mean interval between adjacent members is about $1000\,\mathrm{cm}^{-1}$, appropriate to a C–O stretching mode in a progression, as deduced also for gaseous methanol. This interval is, however, greater than the value $825\,\mathrm{cm}^{-1}$ calculated, or $829\,\mathrm{cm}^{-1}$ observed, for the transition $2\,^1A''–X\,^1A'$ for gaseous methanol [6]. For the next six lines above $70\,000\,\mathrm{cm}^{-1}$, the deduced statures of members, apart from the anomalous line near $71\,800\,\mathrm{cm}^{-1}$, are appropriate to a single progression. Between the first members of the two identified progressions near $66\,350$ and $70\,250\,\mathrm{cm}^{-1}$, the interval is about $4000\,\mathrm{cm}^{-1}$, too large for a C–H stretching mode or a O–H stretching mode. An alternative explanation invokes two separate excited electronic states, of which the first member of each set might mark an origin of an electronic transition; the intensities deduced for members of the second progression, significantly enhanced relative to those of the first progression, support such an assignment. The comparable intensities of the features within each progression are consistent with this premise of two separate electronic states as termini for the transitions, such as $2\,^1A''$ and $3\,^1A''$ or $3\,^1A'$ for gaseous methanol. For methanol in krypton, there is an additional broad absorption in this same region for which there seems no counterpart for gaseous methanol, apart from the broad absorption towards the limit of measurements.

For methanol dispersed in solid argon, we associate a prominent and broad feature centred near $68\,000\,\mathrm{cm}^{-1}$ with the first progression of methanol in krypton, which appears in a region $66\,000–70\,000\,\mathrm{cm}^{-1}$, and a prominent

progression beginning near $73\,500\ \mathrm{cm}^{-1}$ with the second progression of methanol in krypton, beginning in turn near $70\,000\ \mathrm{cm}^{-1}$. The separations between these lines, approximately $850\ \mathrm{cm}^{-1}$, indicate a possible short vibrational progression that might be associated with a C–O stretching mode, as assigned in spectra of gaseous methanol [6] in other regions. For gaseous methanol in this region, all assigned structure seems to pertain to Rydberg series [6], but for molecules in condensed phases such transitions of Rydberg type are typically suppressed or shifted to much greater energies [23]. For this reason we suggest no assignment of these features other than that they likely constitute vibrational structure within an electronically excited state of unknown type. For the four diffuse features centred near $54\,000$, $59\,000$, $64\,000$ and $71\,000\ \mathrm{cm}^{-1}$ for methanol in solid argon, the first of these might be associated with the continuum centred about $55\,000\ \mathrm{cm}^{-1}$ for gaseous methanol, but which is not detected for neat solid methanol; the ratios of intensities are roughly consistent with this attribution. The next two features for methanol in argon might have their counterparts in broad features of methanol in krypton near $60\,000$ and $66\,000\ \mathrm{cm}^{-1}$ respectively, but no particular transition of an isolated molecule seems appropriate. For the fourth feature we suggest no attribution. Although such broad features might result from superimposition of interference fringes on a gradually increasing absorption, the reproducibility of these spectra seems to preclude such an explanation.

The intense and broad features with maxima near $87\,000\ \mathrm{cm}^{-1}$ for methanol in argon and centred about $85\,000\ \mathrm{cm}^{-1}$ for neat solid methanol are likely correlated with the intense absorption beyond $85\,000\ \mathrm{cm}^{-1}$ (cf. Fig. 1) for gaseous methanol that involves ionization, but in lack of both wavenumbers and intensities from calculations we venture no assignment. Comparison of the wavenumbers of the first four broad features deduced for methanol in solid argon with the wavenumbers predicted for vertical excitation of four states $1\ ^1A''$, $2\ ^1A''$, $2\ ^1A'$ and $3\ ^1A''$ of free methanol [6] yields a close agreement for calculations described as TD-DFT (cc-pVTZ), or a similar agreement for calculations described as TD-DFT (cc-pV5Z) with a common shift about $5000\ \mathrm{cm}^{-1}$. Such agreement might be fortuitous because there is no assurance that the environment of solid argon surrounding a dispersed methanol molecule does not perturb substantially the energies, or even the order, of electronic states for that experimental condition relative to the gaseous phase or of a free molecule to which the calculations pertain. The featureless nature of these tabulated absorptions precludes a more definite assignment.

The nature of a sample prepared on slow deposition of a stream of gaseous mixture through its impinging on a surface near 0 K is unknown in detail. Under our experimental conditions, with a substrate cooled to 10 K and for which the cooling power from the refrigerator is approximately 1 W, the incident thermal energy conveyed by the depositing gas is at most 15 mW over an appreciable area, about $5\ \mathrm{cm}^2$; the thin sample has sufficient thermal conductivity to ensure that the temperature at the surface of the deposit as it forms possesses no significant gradient. Visual scrutiny of our solid samples indicates an amorphous nature, with no trace of microcrystalline structure; strong scattering of light in the vacuum ultraviolet region, to which the measurement of an absorption spectrum is sensitive, would analogously indicate a microcrystalline structure, but our experiments present no strong evidence thereof. There is hence no basis for a contention that significant reorganisation of molecules on the surface occurs sufficiently to affect greatly the effective local mean ratio of absorbing species, methanol, to inert diluent, argon or krypton. The proximity of dispersed methanol molecules as a function of intermolecular distance would thus conform to statistical probabilities; for methanol and argon or krypton as roughly spherical and of comparable dimensions, such probabilities of adjacent molecules at nominal molar ratios equal to, or greater than, 200 would thus be less than 1% [24]. Although anomalous intensities of spectral transitions, or their large shifts to smaller differences of energy, of intimately interacting absorbing molecules relative to separate molecules might in principle compensate for the small magnitude on the basis of probability a priori, the spectrum of pure solid methanol proffers no hint of such conditions. The available evidence thus seems to preclude a viable alternative to our spectral analysis above.

5. Conclusion

For samples of methanol either pure or dispersed in solid argon or krypton, all at 10 K, we here report new measurements of their absorption spectra in the vacuum ultraviolet region, upon which we have undertaken a quantitative reduction to distinguish gaussian contributions to the total absorption. By comparison with previously measured spectra of gaseous methanol and with results of quantum-chemical calculations, 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 striking contrast among our spectra of methanol pure and dispersed in argon and in krypton substantiates the value of investigating these phenomena.

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