

Photolysis Cross-Section of Ozone Dimer

I-Cheng Chen,^[a] Andrew F Chen,^[a] Wen-Tsung Huang,^[a, b] Kaito Takahashi,^[a] and Jim J. Lin*^[a, b, c]*Dedicated to Professor Yuan T. Lee on the occasion of his 75th birthday*

Clusters are important in bridging the gap between individual molecules in the gas phase and closely interacting molecules in condensed phases. The size of a cluster is a basic parameter that a researcher would like to control or measure. Whereas the size determination of ionic clusters is rather straightforward, determination of the size of a neutral cluster is much more difficult. Only a few methods are available for the size determination of a neutral cluster beam, including: 1) momentum transfer in crossed-beam scattering,^[1–4] 2) diffraction from a transmission grating,^[5] and 3) high-resolution spectroscopy.^[6–8]

Ozone is not only a crucial molecule in our atmosphere but also a benchmark molecule in photochemistry and photophysics. Theoretical studies on its photodissociation were recently reviewed by Grebenshchikov et al.^[9] Although quite a few excited states and complicated non-adiabatic couplings are involved, high-level theoretical calculations can describe the relevant experimental observables of ozone such as its absorption spectrum, product distributions, etc.^[9–11] The detailed information about the ozone molecule may offer a good starting point for investigations of ozone clusters.

Probst et al.^[12] synthesized the ozone dimer in a molecular beam and probed it with high-resolution electron-impact ionization near threshold. They also performed *ab initio* cal-

culations on the ozone dimer and its possible ionic structures, mostly by means of density functional calculations with the B3LYP functional, and checked the results with a variety of other methods, such as CASSCF and QCISD or CCSD(T). For the neutral ozone dimer, their calculations indicate that two ozone molecules are only very weakly bound to each other. This result also agrees with the small MP2 dimerization energy calculated by Slanina and Adamowicz.^[13]

Bahou et al.^[14] investigated the infrared spectroscopy and photochemistry at 266 nm of the ozone dimer trapped in an argon matrix. The observed frequency shift of the ozone antisymmetric stretching mode upon dimerization is small, about 1 to 3 cm⁻¹, which is similar in magnitude to those induced by different trapping sites in the argon matrix, thus indicating weak interconstituent interactions in the dimer. In their photodissociation experiment, the photolysis cross-section of the matrix-isolated ozone dimer was estimated to be 1.5 × 10⁻¹⁸ cm² at 266 nm,^[14] substantially smaller than the absorption cross-section of the ozone monomer in the gas phase (9.1 × 10⁻¹⁸ cm²).^[15] It should be noted that the photolysis cross-section is the product of the absorption cross-section and the dissociation quantum yield; in the matrix environment the dissociation quantum yield is hard to establish.

Herein, we report the synthesis of ozone clusters in a molecular beam by supersonic expansion. The photolysis cross-sections of the ozone clusters were measured in a mass-resolved manner^[16–19] (with an electron-impact-ionization mass spectrometer) at selected excitation wavelengths (λ). By tuning the temperature and backing pressure before the expansion, we were able to generate ozone clusters of different size distributions. Figure 1 shows typical electron-impact mass spectra of the ozone molecular beam under two expansion conditions. Evidence of cluster formation can be clearly seen: peaks at masses (m/z) 80 (O₅⁺), 96 (O₆⁺), 128 (O₈⁺), and 144 (O₉⁺) indicate that not only the dimer but also larger clusters could be formed. Owing to dissociative ionization in the electron-impact ionization process, the mass 80 peak is the most intense peak other than the monomer mass peaks (O₃⁺, masses 48 and 50). The relative intensities of

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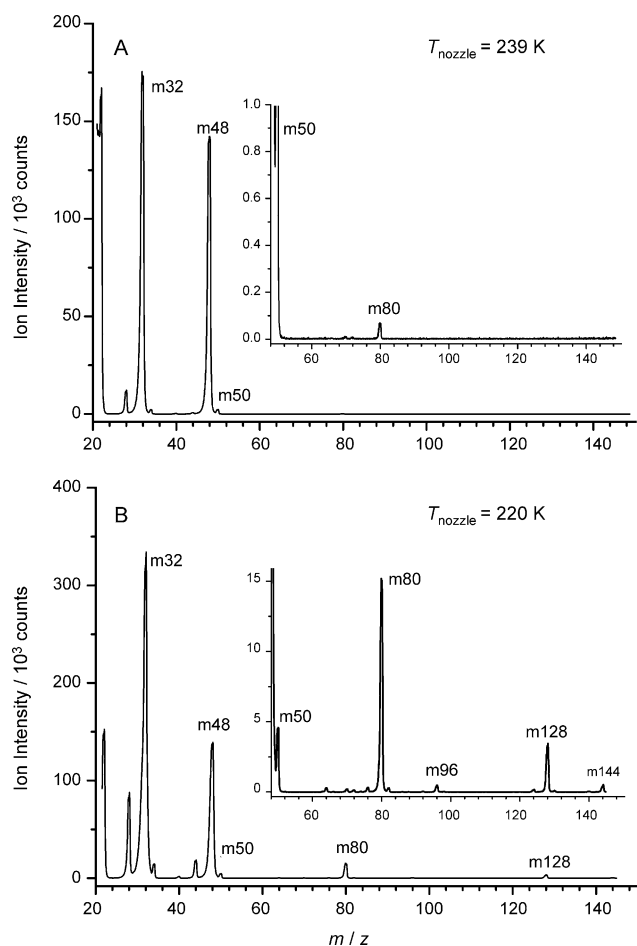


Figure 1. Mass spectrum of the ozone molecular beam seeded in Ne at different nozzle temperatures at a backing pressure of 1.05 bar. a) Nozzle temperature 239 K; b) Nozzle temperature 220 K.

these mass peaks mainly depend on two factors: 1) the population of the cluster sizes and 2) the patterns of dissociative ionization of the clusters.^[1,20] For example, ions of mass 80 may come from the ozone dimer (O_3)₂ and larger clusters and ions of mass 128 may have contributions from the trimer and larger clusters. The formation of large clusters was greatly suppressed at higher nozzle temperatures or at lower backing pressures. For example, by raising the nozzle temperature from 220 to 239 K (Figure 1), most peaks at high masses disappeared; only the peak at mass 80 remained visible among those cluster masses.

Figure 2 shows the molecular-beam photo-depletion signals detected at masses 50 and 80. The signal at mass 50 represents an isotope of the O_3 monomer that mostly consists of one ^{18}O atom (0.2% natural abundance) and two ^{16}O atoms.^[21] Although dissociative ionization of clusters would also contribute to ion signals at masses 48 and 50, the monomer population was overwhelming in our experimental conditions such that the very minor cluster contributions did not affect the photo-depletion signals at masses 48 and 50 at all.

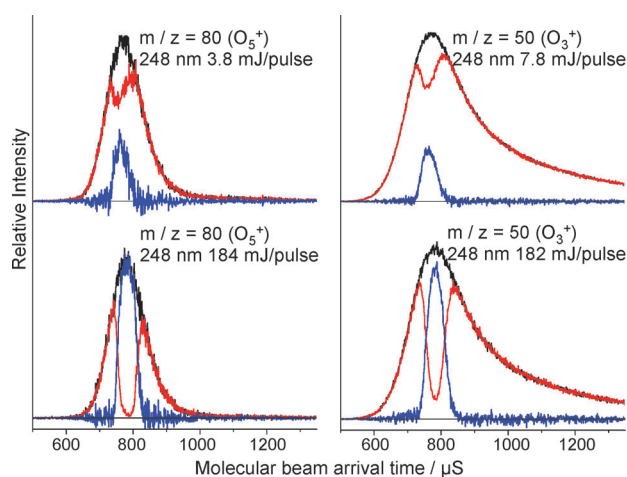


Figure 2. Number-density profiles of the molecular beam showing the photo-depletion signals at two detected masses, $m/z = 50$ and 80 , at different laser energies. Black and red lines are the molecular beam signals before and after laser irradiation (N_2 and N_1), respectively; the blue line is the difference ($N_2 - N_1$).

Under our experimental conditions where the number of photons greatly exceeds the number of molecules, we may write the related kinetic equations as:

$$-\frac{dN}{N_0} = \sigma \phi dI \quad \ln \frac{N_0}{N} = I \sigma \phi \quad (1a)$$

Where N_0 and N are the numbers of molecules before and after the laser irradiation, respectively; I is the laser fluence in number of photons per unit area; σ is the absorption cross-section and ϕ is the dissociation quantum yield. By rearranging [Eq. (1a)], we then have [Eq. (1b)].

$$\frac{N_0 - N}{N_0} = 1 - e^{-I\sigma\phi} \quad (1b)$$

We call $(N_0 - N)$ the laser-depletion signal. [Eq. (1b)] describes a saturation behavior at high laser fluences, that is, the laser-depletion signal $(N_0 - N)$ will converge to N_0 when $I\sigma\phi \gg 1$.

After photo-excitation, the excited states of ozone that are reached are either repulsive or excited above their thresholds, which results in very short lifetimes and complete dissociation to $\text{O} + \text{O}_2$ [$\phi(\text{O}_3) = 1$].^[9-11] For ozone clusters which are only bound by weak van der Waals forces, even if the ejected oxygen atom is blocked by other O_3 molecules, the released energy in the photodissociation is far more than enough to boil off many O_3 molecules. That is, the dissociation quantum yield of an O_3 cluster would not be smaller than that of O_3 . Therefore, we assume $\phi = 1$ in the following discussion.

To avoid confusion, we call the experimental molecular beam signal before laser irradiation N_2 and that after laser irradiation N_1 . Owing to velocity spreads of the molecular beam and other instrument functions, N_2 may be different

from N_0 . For the N_2 time profiles shown in Figure 2, we can see that the time profiles of the cluster (mass 80) are significantly narrower than those of the monomer (mass 50), indicating different velocity distributions. This is due to the fact that dimer and higher clusters only exist at lower temperatures, meaning that they were formed preferentially in the colder central part of the pulsed molecular beam. As a result, the velocity distribution of the cluster is inevitably narrower than that of the monomer. Similarly, the peak shape of the laser-depletion signal N_2-N_1 would also depend on the velocity distribution. In the data analysis, we obtained the numerical values for N_1 and N_2 by integrating the corresponding signals over an arrival time period in which the N_2-N_1 trace (e.g., see Figure 2) shows intensity above the baseline.

An important issue in studying neutral clusters is size determination. Owing to dissociative ionization, the detected m/z value does not necessarily correspond to a definite assignment of the cluster size, but may be used to indicate the cluster formation. Figure 3 shows two saturation curves as a function of laser fluence measured at masses 50 and 80, under an expansion condition where only a very small amount of mass 80 was formed. In Figure 3, the signals at mass 80 saturate at much lower laser fluence than those at mass 50, thus indicating the cross-section observed at mass 80 is larger than that at mass 50. In addition, full saturation can be observed at high laser fluence for both cases. Analysis of the saturation curves with [Eq. (1b)] yielded values of $I\sigma\phi$, and by taking the ratio of the $I\sigma\phi$ values at the two masses, we obtained a cross-section ratio of $\sigma_{m80}/\sigma_{m50}$ (with $\phi=1$). As discussed above, the mass 80 signals may represent the dimer as well as higher clusters, depending on the expansion conditions. To learn more about the cluster size distribution, we performed similar measurements to those in Figure 3 at a number of expansion conditions in which the cluster concentration was varied by large amounts. Here we use the intensity ratio of the two mass peaks (P_{m80}/P_{m50}) as an indicator to represent the relative cluster concentration (cluster/monomer). Under the experimental conditions of Figure 4, the signals at $m/z > 80$ are much smaller than that at $m/z = 80$, thereby, the signal at $m/z = 80$ represents

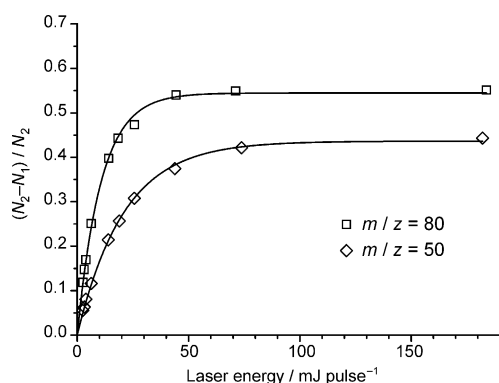


Figure 3. Photo-depletion signals of the ozone monomer ($m/z=50$) and dimer ($m/z=80$) at 248.4 nm. Lines: fit to [Eq. (1b)].

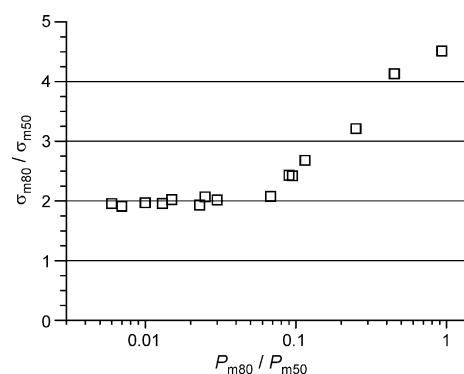


Figure 4. Apparent cross-section ratio at $\lambda=248.4$ nm at different cluster concentrations (indicated by the mass intensity ratio P_{m80}/P_{m50}).

almost all clusters. The apparent cross-section ratio $\sigma_{m80}/\sigma_{m50}$, obtained from signals at masses 80 and 50 is shown in Figure 4, plotted as a function of the cluster concentration indicator (P_{m80}/P_{m50}). We can see that $\sigma_{m80}/\sigma_{m50}$ ratio is about 2 when the cluster concentration is low ($P_{m80}/P_{m50} < 0.07$) and rises very fast to values higher than 4 at high cluster concentrations.

For van der Waals clusters, it is reasonable to presume that the clusters are formed during the expansion of a molecular beam through a build-up process which starts from a dimer, then a trimer, and so on. If this is the case, the most reasonable interpretation of Figure 4 is the following: a dimer is formed first at low cluster concentrations and its cross-section is about twice as large as the monomer cross-section. Larger clusters are formed at higher cluster concentrations and these clusters also contribute to the signal at mass 80 through dissociative ionization; as a result, the apparent cross-section σ_{m80} at a higher cluster concentration is a weighted average of dimer and larger clusters. This observation also implies that the interaction between ozone molecules in the dimer is weak for both ground and excited states, such that the absorption cross-section of the dimer may be described as a simple sum of the constituent ozone molecules. It is worth mentioning that there is a range of expansion conditions ($P_{m80}/P_{m50} < 0.07$), where only the dimer is observed at mass 80. Furthermore, as it is unlikely that the trimer is formed without forming any dimer or that the tetramer is formed without any trimer, there is no step-like structure in Figure 4 at higher cluster concentrations ($P_{m80}/P_{m50} > 0.07$). Unless the ozone dimer was not formed at all in our molecular beam (which is highly unlikely), we believe the above argument is the most reasonable one because we could not think of any other interpretation that can explain all the experimental observations.

It is more interesting to study the cross-section of the ozone dimer at 308.4 nm, which is at the red edge of the strong Hartley band of ozone. A spectral shift caused by interconstituent interactions will appear more clearly at the edges of an absorption band. In practical terms, there was a major difference in our experiments at 308.4 and 248.4 nm: our laser fluence could not saturate the transition at

308.4 nm because the absorption cross-section is much smaller at this wavelength. As a result, we could not perform similar measurements at 308.4 nm to those in Figure 3. Instead, we used [Eq. (2)] to determine the relative cross-section of ozone dimer to monomer:

$$\frac{[\sigma\phi]_{\text{dimer}}}{[\sigma\phi]_{\text{monomer}}} = \frac{I_{\text{monomer}}}{I_{\text{dimer}}} \frac{\ln(N_0/N)_{\text{dimer}}}{\ln(N_0/N)_{\text{monomer}}} \quad (2)$$

where N_0 is the fully saturated laser-depletion signal obtained with [Eq. (1b)] and N is known from the number of molecules (ΔN) depleted by the laser irradiation $\Delta N = N_0 - N = N_2 - N_1$. Owing to the small cross-section and limited laser fluence at 308.4 nm, we could not directly obtain N_0 at this wavelength. To circumvent this difficulty, we used two similar excimer lasers (both were Lambda Physik LPX210i), one operated at 248.4 nm and the other at 308.4 nm, and carefully overlapped the two laser beams so as to have nearly identical interaction volumes with the molecular beam. With a beam flipper (New Focus, Model 9892), we could switch the laser wavelength within a minute. Then we could measure N_0 at 248.4 nm under almost identical molecular beam conditions and use it in the analysis.

The results of the cross-section measurements of the ozone dimer are summarized in Table 1. The unique advantage of our method is that it does not require knowledge of the absolute concentrations. The precision of our measurements is limited solely by the stability of the molecular beam and the laser beam.

Table 1. Summary of the measured photolysis cross-sections of the ozone dimer.

λ [nm]	$\frac{\sigma\phi(\text{dimer})}{\sigma\phi(\text{monomer})}$		σ [10^{-20} cm 2] (monomer) ^[b]	σ [10^{-20} cm 2] (dimer)
	Mean value	Error bar [%] ^[a]		
248.4	1.98	± 4.7	1070	2119
308.4	2.08	± 7.0	10.95	22.78

[a] Relative to the mean value. Error bars: 1 *sigma* (1 standard deviation) and include possible systematic errors like the nonlinearity of the laser power meter, etc. [b] The reference molecule is an isotope of the ozone monomer, $^{30}\text{O}_3$, which has the same cross-section as normal ozone.^[21] The absorption cross-sections of ozone are taken from the JPL 2006 tables.^[15] The dissociation yield of O_3 is taken as unity.

In Table 1 we can see that the cross-section ratio of dimer to monomer at 308.4 nm is 2.08 (± 0.15), also not far from 2. This observation indicates the interconstituent interaction is not strong enough to affect the absorption process of the dimer even at the edge of the Hartley band. To compare the ozone dimer and monomer, we plot the dimer cross-section results together with the absorption spectrum of the ozone monomer^[15,22] in Figure 5. Besides the factor of 2 from the simple sum rule, the dimer shows no significant difference in absorption. The experimental result also indicates that if there is any spectral shift upon the dimerization of ozone, it

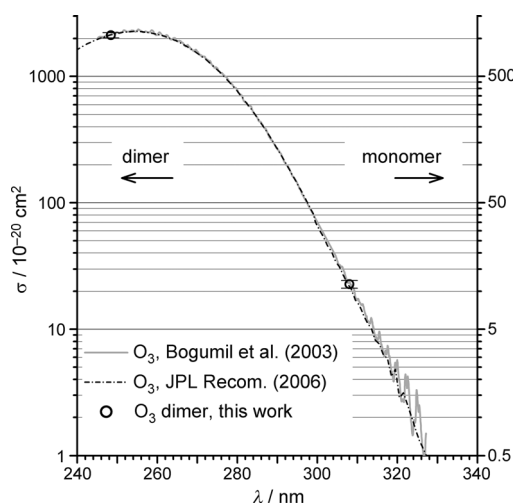


Figure 5. Comparison between the absorption cross-section of the ozone monomer^[15,22] and our molecular beam results for the ozone dimer. Note: For the purpose of easy comparison, the cross-section scales differ by a factor of 2 for the monomer and dimer.

should be less than 1 nm. Moreover, we failed to observe any signal for the photo-depletion of ozone clusters at 351.8 nm (XeF excimer laser) with a similar laser fluence, thus indicating that the cluster cross-section is less than 10^{-20} cm 2 at 351.8 nm (the monomer cross-section is very small at this wavelength,^[15] about 3×10^{-22} cm 2).

The above results indicate that the absorption of the ozone dimer at the Hartley band may be approximated as a sum of two individual ozone molecules. This concept may be applicable to the ozone trimer or larger clusters provided that they also have weak interconstituent interactions. For measuring the size of a molecular cluster, there are only a limited number of methods available which require rather sophisticated instrumentation or analysis. With the cross-section measurement of weakly interacting systems, we may offer a method to determine the average cluster size. It should be noted that this method is only valid at the limit of weak interactions between constituents. In strong interacting systems, the cross-section of a cluster would depend on the coupling of the involved ground and excited states. For example, the calculated absorption spectrum of a water dimer in the \tilde{A} band^[23] exhibits spectral shift and broadening with respect to the monomer, whilst the integrated band intensities per water molecule are about the same for the water dimer and monomer.

To provide theoretical support on the observed 2:1 cross-section ratio between the ozone dimer and monomer, we obtained the electronic vertical transition energy and oscillator strength by CCSD-EOM calculation. With QCISD(T) method, we found many conformers within 1 kJ mol $^{-1}$ of each other for the dimer, including the conformer reported by Probst et al.^[12] and Slanina and Adamowicz.^[13] For this previously reported conformer, two transitions corresponding to the $^1\text{B}_2$ transition of the monomer (responsible for the strong and broad Hartley band) were calculated to be at

5.36 and 5.39 eV with oscillator strength of 0.155 and 0.138, respectively. Therefore it shows that for this conformer the peak position does not change much compared to 5.38 eV for the monomer, and the summed oscillator strength for the dimer is about 1.9 times the monomer value of 0.153. Other low-lying conformers also give summed oscillator strengths of about 1.7 to 1.8 times of the monomer, thereby supporting our experimental finding that the dimer cross-section is approximately twice the monomer cross-section. Theoretical spectral simulation which requires thermal averaging of the nuclear configurations is being pursued and will be reported in the future.

In summary, the ozone dimer has been probed at $m/z = 80$ with conventional electron-impact-ionization mass spectrometry under suitable expansion conditions. Its absorption cross-section has been determined at $\lambda = 248.4$ and 308.4 nm. It may be possible to selectively probe the ozone trimer at a larger mass (e.g., $m/z = 128$, O_3^+) where the ozone dimer does not interfere. The ease of utilizing this method will make it a diagnostic tool when it is required to find suitable conditions for formation of certain clusters.

Experimental Section

The experimental apparatus and method have been described elsewhere.^[16–19,24] The ozone sample was synthesized by flowing O_2 (99.997%, Air Products and Chemicals, Inc.) through a commercial ozonizer, and concentrated with silica gel at 200 K for one hour. The color of the silica gel changed from white to dark purple upon absorbing ozone. After pumping out the oxygen gas, we pre-mixed the purified ozone with neon (ca. 15% ozone) and stored the gas mixture in a 2.5-liter stainless steel cylinder at a low temperature of around 190 K. Decomposition of ozone slowed significantly at those low temperatures, with a lifetime of the ozone mixture of about one day. The molecular beam was formed by flowing the gas mixture through an Even–Lavie valve;^[25] the nozzle was a standard conical nozzle with a full opening angle of 40° and an orifice diameter of 0.25 mm; we controlled the temperature of the valve by adjusting the flow of the nitrogen gas coolant which was pre-cooled using liquid nitrogen. The molecular beam was intersected with a laser beam (KrF, 248.4 nm; XeCl, 308.4 nm;^[26] Lambda Physik, LPX210i) about 35 cm downstream and then detected with an electron-impact quadrupole mass detector another 25 cm downstream from the laser interaction volume. The repetition rate of the molecular beam was 150 Hz and the laser was fired at 75 Hz; therefore, the molecular beam was irradiated by the laser beam every second pulse. To keep the same spatial profile of the laser beam, we used a dielectric-coated variable attenuator (VA248 nm, Laseroptik GmbH) to homogeneously reduce the laser fluence. The laser beam was monitored by a thermopile power meter (Gentec-EO, UP25N).

Computational Methods

We obtained the electronic transition energy and the oscillator strength by performing single-point CCSD-EOM/6–311++G(3df) calculations^[27] using the geometries obtained from the QCISD(T)/6–311++G(3df) method.^[28] All calculations were performed using the MOLPRO program.^[29] For the ozone monomer we obtained an excitation energy of 5.38 eV (230 nm) and oscillator strength of 0.153 for the 1B_2 transition which is responsible for the strong and broad Hartley band observed between 200 and 300 nm. Previous studies by Tachikawa and Abe^[30] and Grebenshchikov et al.^[9] reported transition energies of 5.33 and 4.94 eV, with oscillator strengths of 0.214 and 0.101, using SACCI/6–311++G(d) and MRSDCI/aug-cc-pVTZ, respectively. As our goal is to compare the effect of dimerization on the transition wavelength and intensity, we note

that our oscillator strength of the ozone monomer is in between those two previous reports; we will not elaborate on the differences between the different quantum chemistry methods.

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- [1] U. Buck, H. Meyer, *Phys. Rev. Lett.* **1984**, *52*, 109–112.
- [2] D. Bonhommeau, N. Halberstadt, U. Buck, *Int. Rev. Phys. Chem.* **2007**, *26*, 353–390.
- [3] V. Poterya, V. Profant, M. Farnik, L. Sistik, P. Slavicek, U. Buck, *J. Phys. Chem. A* **2009**, *113*, 14583–14590.
- [4] F. Huysken, M. Kaloudis, A. Kulcke, C. Laush, J. M. Lisy, *J. Chem. Phys.* **1995**, *103*, 5366–5377.
- [5] W. Schöllkopf, J. P. Toennies, *Science* **1994**, *266*, 1345–1348.
- [6] G. Tejada, J. M. Fernández, S. Montero, D. Blume, J. P. Toennies, *Phys. Rev. Lett.* **2004**, *92*, 223401.
- [7] K. Suma, Y. Sumiyoshi, Y. Endo, *Science* **2006**, *311*, 1278–1281.
- [8] F. N. Keutsch, R. J. Saykally, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 10533–10540.
- [9] S. Y. Grebenshchikov, Z.-W. Qu, H. Zhu, R. Schinke, *Phys. Chem. Chem. Phys.* **2007**, *9*, 2044–2064.
- [10] R. Schinke, G. C. McBane, *J. Chem. Phys.* **2010**, *132*, 044305.
- [11] G. C. McBane, L. T. Nguyen, R. Schinke, *J. Chem. Phys.* **2010**, *133*, 144312.
- [12] M. Probst, K. Hermansson, J. Urban, P. Mach, D. Muigg, G. Denifl, T. Fiegele, N. J. Mason, A. Stamatovic, T. D. Mark, *J. Chem. Phys.* **2002**, *116*, 984–992.
- [13] Z. Slanina, L. Adamowicz, *J. Atmos. Chem.* **1993**, *16*, 41–46.
- [14] M. Bahou, L. Schriver-Mazuoli, A. Schriver, *J. Chem. Phys.* **2001**, *114*, 4045–4052.
- [15] S. P. Sander, B. J. Finlayson-Pitts, R. R. Friedl, D. M. Golden, R. E. Huie, H. Keller-Rudek, C. E. Kolb, M. J. Kurylo, M. J. Molina, G. K. Moortgat, V. L. Orkin, A. R. Ravishankara, P. H. Wine, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies 06–2*, Jet Propulsion Laboratory, Pasadena, **2006**.
- [16] H.-Y. Chen, C.-Y. Lien, W.-Y. Lin, Y. T. Lee, J. J. Lin, *Science* **2009**, *324*, 781–784.
- [17] C.-Y. Lien, W.-Y. Lin, H.-Y. Chen, W.-T. Huang, B. Jin, I.-C. Chen, J. J. Lin, *J. Chem. Phys.* **2009**, *131*, 174301.
- [18] B. Jin, I.-C. Chen, W.-T. Huang, C.-Y. Lien, N. Guchhait, J. J. Lin, *J. Phys. Chem. A* **2010**, *114*, 4791–4797.
- [19] J. J. Lin, A. F. Chen, Y. T. Lee, *Chem. Asian J.* **2011**, *6*, 1664–1678.
- [20] O. Kornilov, J. P. Toennies, *J. Chem. Phys.* **2008**, *128*, 194306.
- [21] We chose to monitor the ozone monomer at a mass of 50, instead of its most abundant mass 48, simply because the signal at mass 48 was too large (our ion counting system was saturated) under the expansion conditions where ozone clusters could be formed. To check whether the absorption cross-section of ozone depends on the isotopes, we measured the photo-depletion signals at masses 48 and 50 under expansion conditions where signals at both masses did not saturate our detection system. The results showed almost identical laser-depletion signals, thereby indicating that the absorption cross-section of ozone is the same for these two isotopes (masses 48 and 50) at 248.4 nm.

- [22] K. Bogumil, J. Orphal, T. Homann, S. Voigt, P. Spietz, O. C. Fleischmann, A. Vogel, M. Hartmann, H. Bovensmann, J. Frerick, J. P. Burrows, *J. Photochem. Photobiol. A* **2003**, *157*, 167–184.
- [23] G. Avila, G. J. Kroes, M. C. van Hemert, *J. Chem. Phys.* **2008**, *128*, 144313.
- [24] J. J. Lin, D. W. Hwang, S. Harich, Y. T. Lee, X. Yang, *Rev. Sci. Instrum.* **1998**, *69*, 1642–1646.
- [25] U. Even, J. Jortner, D. Noy, N. Lavie, C. Cossart-Magos, *J. Chem. Phys.* **2000**, *112*, 8068–8071.
- [26] D. M. Wilmouth, T. F. Franco, R. M. Stimpfle, J. G. Anderson, *J. Phys. Chem. A* **2009**, *113*, 14099–14108.
- [27] a) H. Koch, P. Jørgensen, *J. Chem. Phys.* **1990**, *93*, 3333–3344;
b) J. F. Stanton, R. J. Bartlett, *J. Chem. Phys.* **1993**, *98*, 7029–7039;
c) H. Koch, R. Kobayashi, A. Sánchez de Merás, P. Jørgensen, *J. Chem. Phys.* **1994**, *100*, 4393–4400.
- [28] J. A. Pople, M. Head-Gordon, K. Raghavachari, *J. Chem. Phys.* **1987**, *87*, 5968–5975.
- [29] MOLPRO, version 2010.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, F. R. Manby, M. Schütz, and others, see <http://www.molpro.net>.
- [30] H. Tachikawa, S. Abe, *Chem. Phys. Lett.* **2006**, *432*, 409–413.

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