

Infrared laser multiple photon ionization

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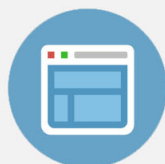
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Infrared laser multiple photon ionization

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The production of ions as a result of the interaction of intense CO₂ laser pulses with a variety of organic molecules is reported. The laser frequency dependence of the ionization follows closely the linear infrared absorption spectrum of the respective molecule. The extent of ionization depends very strongly on laser energy fluence. The ion-production process is found to have a strongly collisional character. Various possible mechanisms of laser-induced ionization are discussed, and evidence is presented favoring laser-induced chemi-ionization.

I. INTRODUCTION

The number of chemical reactions known to be induced by infrared lasers as a result of multiple-photon absorption is constantly increasing.¹⁻³ Two different general types of reactions have been studied: (i) homolytic dissociations and (ii) isomerizations. Both types of reactions produce electrically neutral products. In addition, however, there have been some reports regarding the observation of charged species produced by the action of intense CO₂-laser beams on polyatomic molecules. Specifically ions have been observed in BCl₃,^{4,5} H₂O,⁶ D₂O,⁷ SiF₄,⁸ and SiH₄.⁹ Despite the intrinsic interest in the phenomenon and its suggested potential use for electric isotope separation,⁴ the mechanism of ionization is still unknown. Particularly puzzling is the report by Chin and Faubert⁷ that the ionization of D₂O takes place at CO₂-laser frequencies not resonantly absorbed by the molecule.

In a recent communication¹⁰ we reported the production of ions as a result of the interaction of intense CO₂-laser pulses with an organic molecule, CH₃NO₂. In this paper we present more extensive studies. Ion production is found in a variety of organic molecules. The dependence of the ionization on laser frequency and power and on parent molecule pressure is investigated, and the possible mechanisms responsible for the ionization are analyzed.

II. EXPERIMENTAL

In our previous experimental setup,¹⁰ the ionization of molecules was detected using a simple parallel-plate ionization cell filled with the static gas. In the present work, a different apparatus was constructed allowing one to look for ionization in the mTorr range by direct ion counting. The apparatus consisted of a two-chamber vacuum system differentially pumped through a 1 mm hole. The CO₂-laser beam (0.4 J, 5 Hz, multimode) was focused by a 5 cm f.l. BaF₂ lens at the center of a pair of parallel-plate electrodes, 50 mm in diameter and 12 mm apart. One of the electrodes served as the partition of the two vacuum chambers and contained the 1 mm hole. The other (driving) electrode was designed⁷ in order to minimize secondary ion formation. The electrode was driven by a high voltage pulser (Velonex

350). In a typical experiment, a 0.5–2 μsec long voltage pulse of 200–600 V was applied immediately after the CO₂-laser pulse. Ions passing through the 1 mm hole and a copper shield at liquid N₂ temperature were detected by a Spiraltron detector (Galileo 4219X). The electric pulses from the Spiraltron were amplified and discriminated by a Pacific Photometrics AD-6 unit and counted by a gated counter (Ortec 772).

Both chambers had base pressures below 5×10^{-7} Torr. Experiments were conducted with a rapid gas flow through the sample chamber in order to avoid the accumulation of reaction products.

While the apparatus was designed primarily for ion counting at low pressure, with proper modifications the sample chamber can also be used as a parallel plate ionization cell for high pressure measurements. The advantages of this over our previous ionization cell¹⁰ are (a) much lower base pressure and (b) rapid gas flow. In this configuration, the conductivity pulses were amplified (Tektronix 1A7A) and averaged by a waveform acquisition system (Tektronix 4051/7912AD). Data in the pressure range 1–10 Torr were taken using this system.

All the gases were Research Grade (Matheson), while the other chemicals (Aldrich) were either Spectrophotometric Grade or of the highest available purity.

III. RESULTS

A. High pressure behavior

Eight different molecular systems were studied to determine if ionic species are formed by the action of the CO₂ laser. Specifically, these were nitromethane (CH₃NO₂), methanol (CH₃OH), vinylcyanide (CH₂CHCN), ethylene (C₂H₄), dihydropyran (C₄H₆O), ethyl-vinyl-ether (C₂H₅OC₂H₃), cyclopropane [(CH₂)₃], and ammonia (NH₃). All these molecules have been studied in the past and were found to undergo CO₂-laser induced multiphoton dissociation. Our studies showed that all but the last two molecules give ionic products.

In all cases where ionization was observed, the excitation spectrum for ion production was found to correlate well with the linear infrared absorption spectrum of the particular molecule. No significant shifts were observed. Figures 1–3 show the corresponding spectra for CH₃NO₂, CH₃OH, and CH₂CHCN. The published¹¹ optoacoustical and infrared multiple-photon dissociation (IRMPD) product luminescence action spectra for CH₃NO₂ agree well

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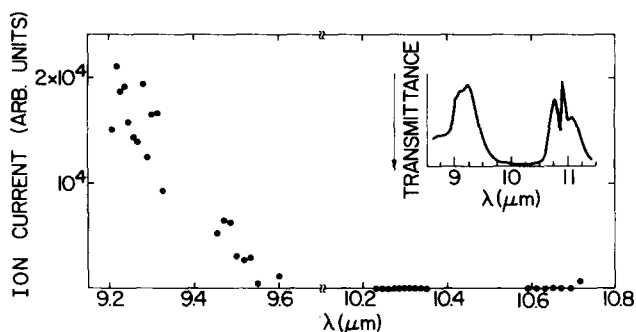


FIG. 1. Nitromethane: Ion current vs CO_2 -laser wavelength. CH_3NO_2 pressure: 10 Torr; laser-pulse energy: 105 mJ; external bias: 14 V. Each point represents the average of 64 laser shots. Inset: The linear infrared absorption spectrum of CH_3NO_2 .

with our ion-production spectrum. The tunability excludes the possibility that observed ionization is simply a result of a dielectric breakdown process brought by the laser radiative heating (inverse bremsstrahlung) of free electrons in the sample. Laser-induced breakdown accompanied by strong luminescence was observed at high pressures (> 50 Torr). CH_2CHCN is interesting in that excitation of the much weaker $9 \mu\text{m}$ band gives about the same ionization as the strong $10 \mu\text{m}$ band using the same laser pulse energy and the same pressure.

Further studies were conducted on the easily ionizable and simpler molecules CH_3NO_2 , CH_3OH , CH_2CHCN , and C_2H_4 . The dependence of the ionization current (I_{ion}) on laser pulse energy (E_p) was found to be very steep. For example, for CH_3NO_2 , $I_{\text{ion}} \propto E_p^{4.5}$; for CH_3OH , $I_{\text{ion}} \propto E_p^{3.5}$, and for C_2H_4 , $I_{\text{ion}} \propto E_p^{4.5}$. In CH_3NO_2 the dependence is found to be the same in both the 9 and $10 \mu\text{m}$ bands. This is not, however, the case for CH_2CHCN ; Fig. 4 shows the results.

Finally, the dependence of I_{ion} on parent molecule

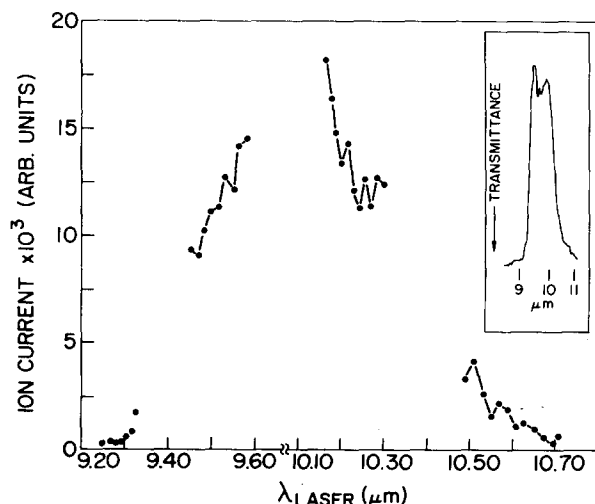


FIG. 2. Methanol: Ion current vs CO_2 -laser wavelength. CH_3OH pressure: 10 Torr; laser-pulse energy: 200 mJ; external bias: 150 V. Each point represents the average of 64 laser shots. Inset: The linear infrared absorption spectrum of CH_3OH .

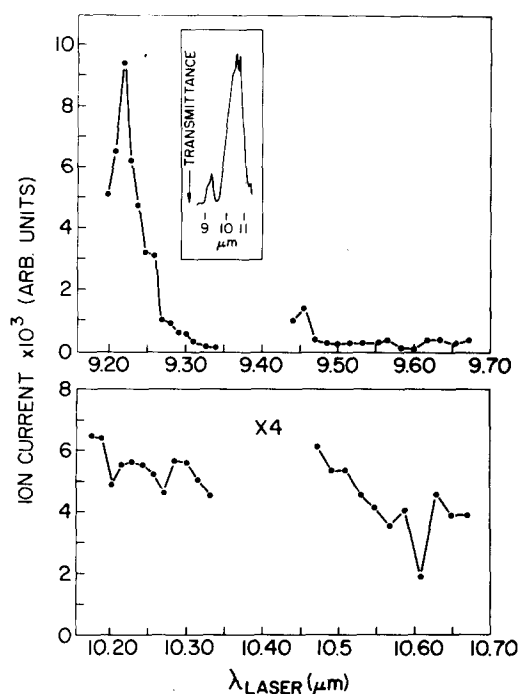


FIG. 3. Acrylonitrile: Ion current vs CO_2 -laser wavelength. The ionization spectrum in the $9 \mu\text{m}$ region was obtained at a CH_2CHCN pressure of 10 Torr, while the $10 \mu\text{m}$ spectrum was obtained at a pressure of 5 Torr. Laser pulse energy: 200 mJ; external bias: 150 V. Each point represents the average of 64 laser shots. Inset: The linear infrared absorption spectrum of CH_2CHCN .

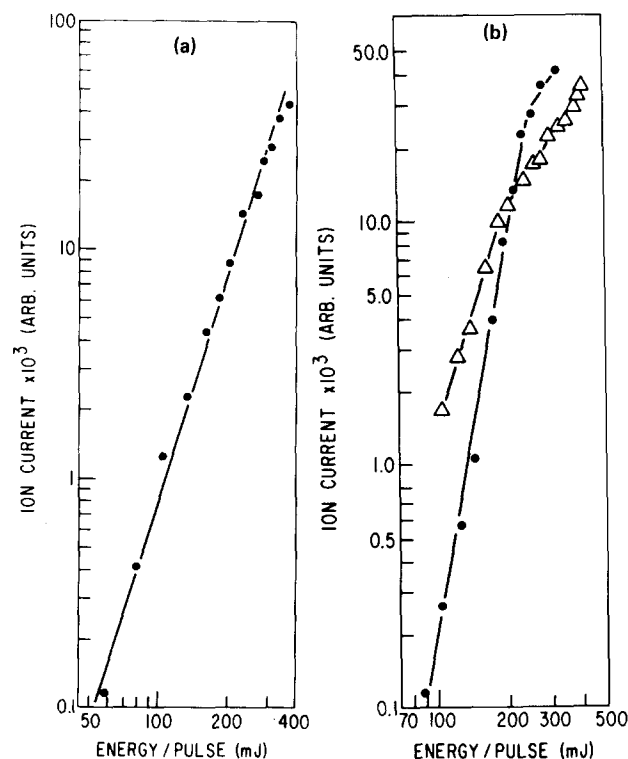


FIG. 4. Laser-pulse-energy dependence of the ion current. (a) 10 Torr of CH_3OH excited by the $R(18)$ line of the $10 \mu\text{m}$ band. (b) 10 Torr of CH_2CHCN excited by the $R(32)$ line of the $9 \mu\text{m}$ band (circles), or by the $R(24)$ line of the $10 \mu\text{m}$ band (triangles). Each point represents the average of 64 laser shots.

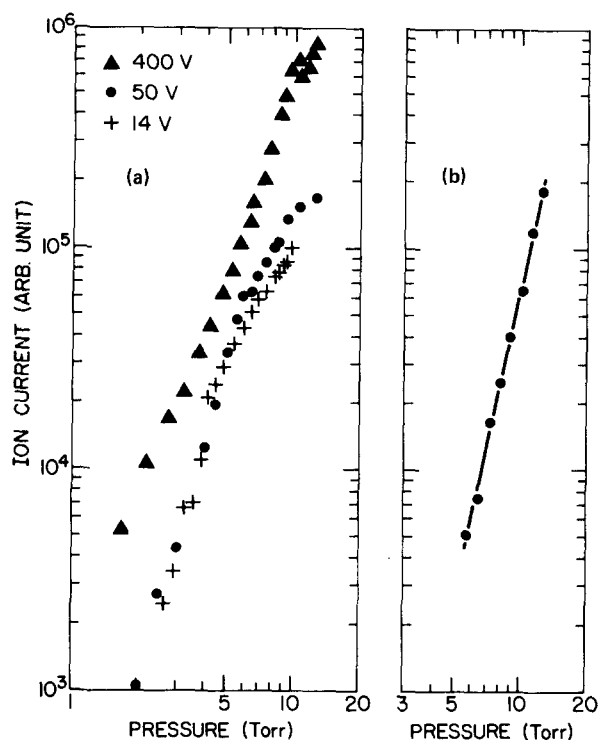


FIG. 5. Parent molecule pressure dependence of the ion current. (a) CH_3NO_2 excited by the $R(24)$ line of the $9\ \mu\text{m}$ band. Laser-pulse energy, 130 mJ. The external bias on the ionization cell plates varies as follows: triangles, 400 V; circles, 50 V; and crosses, 14 V. (b) Ethylene excited by the $P(20)$ line of the $10\ \mu\text{m}$ band. Laser-pulse energy: 130 mJ; external bias: 14 V. Each point represents the average of 64 laser shots.

pressure (P) was studied. It was found to be very steep and dependent on the magnitude of the dc voltage applied between the parallel plates. For CH_3NO_2 , with a dc voltage of 500 V, $I_{\text{ion}} \propto P^{2.5}$, while for 50 and 14 V, $I_{\text{ion}} \propto P^4$ (Fig. 5). Saturation effects also appear in the high pressure range and are more important at low voltage.

B. Low pressure behavior

The low pressure behavior (10^{-5} – 10^{-3} Torr range) was investigated by utilizing the apparatus described in Sec. II. The ion-detection capability of the setup was tested by recording the multiphoton ionization (MPI) spectra of triethylenediamine. A Nd^{3+} :YAG laser pumped dye laser was used as the excitation source. Strong ionization at the focal volume of the laser beam was observed at pressures as low as 1 mTorr, and the MPI spectrum was identical to that published by Parker and Avouris.¹² With CO_2 -laser irradiation, we have looked for ionization in two different gases, namely, CH_2CHCN and CH_3OH , since these molecules produce the strongest ionization signals at high pressure. Due to the differential pumping capacity of our apparatus, the highest sample pressure was limited to <10 mTorr. Despite our many attempts, no ionization could be detected in either of the samples, in the pressure range of 10^{-5} – 10^{-2} Torr.

IV. DISCUSSION

The results presented in Figs. 1–5, obtained in the high pressure range (1–10 Torr), suggest that the ionization process involves a multiphoton vibrational absorption process resonant in the first photon. However, as the results on CH_2CHCN show (Figs. 3 and 4) the linear infrared absorption is not the sole factor determining the ionization efficiency. As it can be seen, excitation of the $9\ \mu\text{m}$ band leads to a more facile up-pumping even though the linear absorption cross section is smaller for $9\ \mu\text{m}$ than for $10\ \mu\text{m}$ radiation. An analogous behavior has been reported earlier by Am-bartzumian *et al.*¹³ in the case of the IRMPD of CCl_4 .

The pressure dependence of the ionization process is very informative. The observed variation with the applied dc voltage can be understood if we consider that the observed pressure dependence of I_{ion} at high dc fields is a convolution of the pressure dependences of the ionization process itself and of the dominant subsequent electron multiplication under the influence of the external field. The saturation at high pressure reflects the ability of the external field to collect all the produced charge carriers. In our previous paper on this subject,¹⁰ we studied the pressure dependence of the ion current with the ionization cell plates biased to 200 V, i.e., under strong multiplication conditions. Under these conditions we found that for CH_3NO_2 , $I_{\text{ion}} \propto P^{3.3}$. The increased sensitivity of our experimental setup allowed us to conduct the measurements with a low external bias. At low dc voltage, 14 V, electron multiplication does not take place. This is because the ionization potential of CH_3NO_2 is 11.3 eV,¹⁴ while the charge carrier diffusion is ambipolar giving about 0.6 cm acceleration path. In the absence of electron multiplication processes the observed pressure dependence reflects the intrinsic pressure dependence of the ionization process, which is therefore found to be strongly collisional in nature. The very strong pressure dependence of P^4 evidently continues down to lower pressure range since no ionization could be detected at a pressure of a few mTorr.

The mechanism by which collisions affect the fractional ion yield may be physical, e.g., a change in the cross section for multiple-photon absorption induced by pressure broadening or rotational cross relaxation, or it may be chemical, i.e., ions may be produced as a result of high order chemical reactions.

A. Direct ionization

A mechanism of CO_2 -laser induced ionization according to which the molecule acquires, through vibrational excitation, enough energy to match its ionization potential (IP) was first suggested by Akulin *et al.*⁴ Such a mechanism involves climbing up the vibrational ladder of the ground state, crossing to the first excited electronic state (an inverse internal conversion process) and continuing the ascent up the different electronic states to reach the ionization continuum. The efficiency of such a mechanism will depend on a variety of factors, such as the vibrational structure of the different electronic states, the coupling between them and the magni-

tude of the IP. The last parameter does not appear, however, to be an important factor in our experiments since molecules that both give and do not give ions have IP's in the range of 10–11 eV. Reverse internal conversion has been detected through the observation of prompt luminescence in certain cases^{15–17}; however, the requirements for ionization are more demanding. The principal objection to a direct ionization mechanism is the requirement that a large amount of energy, typically 10 eV, has to be deposited in the molecule in a very short period of time. As the molecule climbs up to higher energy states, it encounters different dissociative states (typical dissociation energies 3–5 eV), and the rate of chemical decay through these channels increases drastically with excess energy above the activation energy threshold.¹⁸ The laser up-pumping rate should therefore be able to compete with the increasing rates of chemical decay and with the rates of radiative decay of the electronically excited states. From the available data on a variety of molecules,¹ only modest excess excitations (up to ~10 i.r. photons) above the lowest energy reaction threshold can be attained. It does not appear therefore that direct ionization is a realistic mechanism for ion production.

B. Ionic dissociation

All the studies of IRMPD reported up to the present involve the homolytic fission of a chemical bond to give two neutral fragments, i.e., $AB \rightarrow A + B$. In principle, an ionic dissociation channel also exists, e.g., $AB \rightarrow A^+ + B^-$. Chin⁶ has in fact suggested this process as a possible mechanism for the production of ions upon CO_2 -laser irradiation of H_2O . However, since, in general, the typical electron affinities of organic molecules are lower than the ionization potentials, these ionic channels lie at much higher energies than the neutral channel.

A simple calculation gives an idea of the energies involved for the formation of separated ionic fragments. For CH_3OH , given that the $\text{CH}_3\text{--OH}$ bond energy is 3.9 eV, the CH_3 radical ionization potential is 9.9 eV, and the OH electron affinity is -1.8 eV, then the $\text{CH}_3\text{OH} \rightarrow \text{CH}_3^+ + \text{OH}^-$ channel is estimated at 12 eV. This value is in fact higher than the IP of CH_3OH , 10.9 eV. Analogous results are obtained for the rest of the molecules. For H_2O the situation is even more unfavorable since the channel $\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+$ is estimated to lie at ~17 eV. Although these calculations are, of course, only indicative, they show that in the gas phase, without the stabilizing effects of polar dielectrics, ionic channels are not likely to be reached.

In addition to the general arguments against direct ionization or ionic dissociation, our experimental data argue against these mechanisms. If either of these mechanisms were dominant, we would have detected ions at low pressure. Our negative finding shows that, in our experiment, the mechanism of ionization is strongly collisional.

C. Chemi-ionization

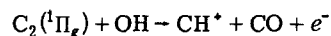
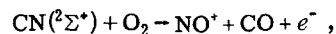
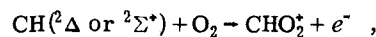
Chemi-ionization is defined¹⁹ "as a process by which the number of elementary charge carriers is increased

as a direct result of the formation of new chemical bonds." In our case, chemi-ionization can be realized through reactions of free radicals, produced as primary or secondary products of the IRMPD process with the parent compound itself or with other fragments. The reaction should be exothermic enough so that ionization of one of the products is accomplished with minimal or no external energy input. The reactants could be both in their electronic ground state or one of them could be electronically excited. The latter situation is obviously energetically more favorable for chemi-ionization.

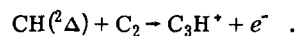
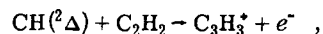
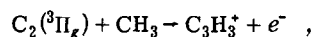
Most of the literature on chemi-ionization involves associative ionization reactions between excited atoms or between atoms and diatomic molecules. A more relevant area to us is chemi-ionization observed in the combustion of organic compounds. As early as 1906, Tufts²⁰ suggested that ions in hydrocarbon flames resulted from the chemistry of the combustion process and were not solely thermal in origin. A variety of chemi-ionizing reactions have been proposed involving carbon containing radicals ca. CH and C_2 and oxygen species ca. O, OH, and O_2 .

The study of the IRMPD of the molecules investigated in this paper has shown the presence of the same free radicals proposed as responsible for chemi-ionization in combustion. For example, in the case of IRMPD of CH_3NO_2 , several excited diatomic fragments were detected^{21,22}: $\text{CN}(\tilde{B}^2\Sigma^+)$, $\text{CH}(\tilde{A}^2\Delta)$, $\text{C}_2(\tilde{d}^3\Pi_g)$, $\text{O}_2(\tilde{A}^3\Sigma_u^-)$, and $\text{OH}(\tilde{A}^2\Sigma^+)$. In addition NO_2 and $\text{NO}^+(\text{CH}_3)$ should also be present) were detected.²² Analogous fragments have been detected in the IRMPD of the other molecules. For example, we use the case of CH_3OH : OH^* , CH^* , C_2^* (CH_3 should also be present) have been detected^{23,24} along with stable molecules such as C_2H_4 and C_2H_2 .

Several chemi-ionizing reactions involving the above fragments can be written. Some of the reactions originally suggested^{25,26} as involved in ion production in flames such as



could be involved. Oxygen is not absolutely necessary, and chemi-ionization involving only hydrocarbon species has been found in pyrolysis. Proposed reactions^{27,28} include



However, chemi-ionization during the pyrolysis of hydrocarbons is less efficient than in flame systems.²⁹ In flame systems, themselves, the ion yield is very low; one ion is produced per ~10⁶ C atoms oxidized. We note that all the systems we studied which gave strong ionization as a result of CO_2 -laser irradiation contain heteroatoms O or N. Therefore, reactions analogous to the ones involved in flames could take place. When 150 mJ CO_2 -laser pulses are focused by a 10 cm lens

into 10 Torr of CH_3NO_2 about 10^5 ions/pulse are produced. Under the same conditions and after correcting for differences in linear absorption cross section, the ionization in C_2H_4 is down by a factor of ~ 40 .

The observed high pressure dependence of the ionization current is consistent with this picture of chemi-ionization. We have been able to monitor the luminescence intensity (I_L) from certain radicals resulting from the IRMPD of CH_3NO_2 as a function of pressure.²² At $P > 0.5$ Torr the pressure dependence is approximately quadratic, namely, $I_L(\text{CN}) \propto P^2$, $I_L(\text{CH}) \propto P^{2.3}$, and $I_L(\text{NO}_2) \propto P^{1.7}$. These results indicate that the $I_{\text{ion}} \propto P^4$ dependence in CH_3NO_2 is reasonable for a bimolecular chemi-ionizing reaction involving free radicals.

The above picture of laser-induced chemi-ionization is further supported by an experiment by Crim *et al.*³⁰ In that experiment, ionization as a result of the interaction of intense CO_2 -laser pulses with SF_6 -hydrocarbon mixtures was observed. Since SF_6 alone does not lead to ionization, it was proposed that the vibrationally excited SF_6 somehow induces the fragmentation of the hydrocarbons, and the resulting fragments lead to chemi-ionization.

Carbon-containing radicals are not necessary for chemi-ionization, and therefore the IRMPD of inorganic molecules could also lead to ionization. In the case of NH_3 we have not observed any ionization. The products of the IRMPD of NH_3 are $\text{H}(1^2\text{S})$, $\text{NH}_2(\tilde{X})$, and to a small extent $\text{NH}_2(\tilde{A})$,^{31,32} and with these products no chemi-ionization seems possible. However, in the case of the hydride SiH_4 , Deutsch⁹ has reported ionization with a yield of $\sim 10^{-6}$. The IRMPD of SiH_4 was accompanied⁹ by strong H-atom Balmer emission and H_2 molecular emission. (We have verified independently the above emission results.) Given the observed emissions, chemi-ionization is certainly a possibility in the case of SiH_4 through reactions such as³³ $\text{H}_2^* + \text{H}_2 \rightarrow \text{H}_3^* + (\text{H} + e^-)$ and $\text{H}(2^2\text{S}) + \text{H}_2 \rightarrow \text{H}_3^* + e^-$.

Although chemi-ionization appears to be the most probable cause for the ionization we have observed, our data cannot identify the particular chemi-ionization processes involved. Mass-resolved ion-detection techniques would be particularly useful in this respect. However, it should be noted that it is not always easy to identify the primary ionic products because of subsequent, very efficient ion-neutral reactions which lead to a variety of ionic products.

In addition to chemi-ionization, thermal ionization of the molecules M represented by the equilibrium $M \rightleftharpoons M^+ + e^-$ could in principle contribute to the observed ionization. The temperature dependence of such an ionization process is described by the well known Saha equation.³⁴ In our case, the final temperature of the system cannot be calculated accurately, due to the absence of information regarding the amount of energy deposited within the focal volume of the beam. However, the expected temperatures do not exceed a few thousand degrees. Under these conditions, molecular dissociation processes, which are the precursors of chemi-ionization, are expected to predominate over electron

production. In terms of the Saha theory, this is a result of the higher entropic contribution of translational motion by the heavy fragments compared to that by the electron.³⁵

V. CONCLUSIONS

We have shown that the appearance of ionic species as a result of the interaction of high power CO_2 -laser beams with polyatomic molecules is a wide spread phenomenon. The interaction involves multiple-photon vibrational absorption resonant in the first photon. However, the linear absorption cross section for the first photon is not the sole factor controlling the absorption process. The ion-production process(es) is found to be collisional in nature. No ions are detected in the collision-free pressure regime. A mechanism consistent with the findings involves infrared multiphoton dissociation of the parent molecule to give radical species, possible secondary photofragmentation of these species, and finally chemi-ionization through reactions of the radicals. Direct ionization to give the parent ion or ionic dissociation of bonds as a result of multiphoton vibrational absorption does not appear to be possible. It was previously suggested⁴ that the CO_2 -laser induced ionization could be used for electric isotope separation. This task will not be realizable because the collisional nature of the process will tend to scramble the isotopic species and, of course, the ion yield is very low. However, with appropriate instrumentation such as mass-resolved detection of the ions, laser-induced chemi-ionization could become a powerful approach in the study of molecular chemi-ionization processes.

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