

MULTIPHOTON IONIZATION: A METHOD FOR CHARACTERIZING MOLECULAR BEAMS AND BEAM REACTION PRODUCTS*

D.L. FELDMAN, R.K. LENGEL** and R.N. ZARE**

*Department of Chemistry, Columbia University,
New York, New York 10027, USA*

Received 3 August 1977

The technique of multiphoton ionization is applied to Na_2 in an effusive and a supersonic beam to characterize the internal state distribution of this molecule. A tunable dye laser is swept through the wavelength region of the Na_2 B-X system and positive ions are counted as a function of laser wavelength. Multiphoton ionization involving a real intermediate state is also used to characterize the BaCl product formed in the beam-gas reaction $\text{Ba} + \text{HCl}$. This detection system can combine mass spectrometry with laser spectroscopy for the identification and characterization of beam species. Advantages and drawbacks are discussed.

1. Introduction

With the increased interest in state specific rather than bulk kinetic information, it has become necessary to refine detection techniques [1]. The most commonly used methods are spectroscopy, such as time-resolved absorption, infrared chemiluminescence, or laser-induced fluorescence [2]. These spectroscopic techniques observe the disappearance/appearance of light from the matter-radiation interaction. An alternative procedure is to observe the modification of the matter target. This latter possibility is particularly appealing when the charge-to-mass ratio is altered, such as the conversion of a neutral to an ionic species, or the conversion of one ionic species to another of different mass or charge. Then one can apply mass spectrometric detection in which the ions of a different charge-to-mass ratio are counted. We report here the use of multiphoton ionization (MPI) to study two different systems: the characterization of Na_2 formed by supersonic expansion of sodium vapor and of BaCl formed in the reaction $\text{Ba} + \text{HCl}$ under single-collision conditions.

MPI is made possible by the advent of high-power lasers that can induce an atom or molecule to absorb more than one photon. The probability for multiphoton ionization is enormously enhanced by the existence of a real level, E'_k , that lies above the initial level, E_0 , at an energy equal to an integral multiple of the photon energy. Such a level is called a quasi-resonant level and satisfies the condition that $E'_k - E_0 \approx nh\nu$. By recording the ion count versus the wavelength of a tunable dye laser, an MPI spectrum is generated. Past applications of MPI, involving real intermediate states, have concentrated on obtaining spectroscopic information on atomic [3-7] and molecular [3,8-11] systems. The present studies are motivated instead by the possibility of using MPI as a beam diagnostic.

2. Experimental setup and results

2.1. Na_2 beam species

The output from a nitrogen-pumped (≈ 5 pps) tunable dye laser (Molelectron D1-200) crosses at right angles a molecular beam. A 2" focal length lens is used to focus the laser upon the interaction region. A channeltron (Ceratron E from Murata Corp.) that is wired to collect positive ions is placed perpendicular to and

* Support by the National Science Foundation is gratefully acknowledged.

** Present address: Department of Chemistry, Stanford University, Stanford, California 94305, USA.

8 cm above the plane formed by the two intersecting beams. The signal is amplified ($2 \text{ V}/\mu\text{A}$), then processed through a boxcar integrator (PAR model 162) with a 1 s observed time constant.

The beam apparatus has been described elsewhere [12]. A nozzle beam source is used in conjunction with liquid-nitrogen-cooled collimators. An aluminum chamber surrounds the interaction region. This is superior to a glass chamber since the latter collects ions on its insulating surface, causing interference with the signal. A plate biased at 90 V is placed before the intersection region; it serves to suppress the ion background.

The MPI spectra for sodium dimers both before and after expansion are shown in fig. 1. The simplification of the structure due to cooling is obvious. Only lines originating from $v'' = 0, 1$ (and with amplification, $v'' = 2$) levels are observed. The signal-to-noise ratio is about 20 to 1, much of the noise being caused by fluctuations in the excitation source.

The lowest ion channel for Na_2 is direct two-photon ionization at $4.94 \pm 0.1 \text{ eV}$ [13]. The next ion channel is pair production, $\text{Na}^+ + \text{Na}^-$. Using $1.1 \pm 0.1 \text{ eV}$ for the dissociation energy of Na_2^+ [13], and $0.548 \pm 0.004 \text{ eV}$ for the electron affinity of Na [14], this channel is estimated to lie about $0.55 \pm 0.1 \text{ eV}$ above $\text{Na}_2^+ + e^-$. A study of the time evolution of the (1, 0) signal showed only one peak for this band. We interpret this peak at 4900 \AA (2.52 eV) to be Na_2^+ on energetic grounds.

There are some peculiarities of the MPI spectrum that should be pointed out. For an n th order ionization process, one might naively expect that the number of ions formed is proportional to the laser intensity raised to the n th power. The above model then predicts that the Na_2^+ signal has a quadratic dependence on the laser power ($n = 2$). We find instead a linear dependence that persists as the laser intensity is decreased.

It is also interesting to note that the relative signal strength of the bands are not in the ratio of their Franck-Condon factors but instead simply follow the laser intensity, as shown in fig. 2. For example, the intensity of the (1, 0) band to the (0, 0) band is 0.95, although the ratio of the respective Franck-Condon factors [15] is 2.5.

We also find that the MPI spectrum is not consistent with the temperature studies done by Sinha et al. [12]

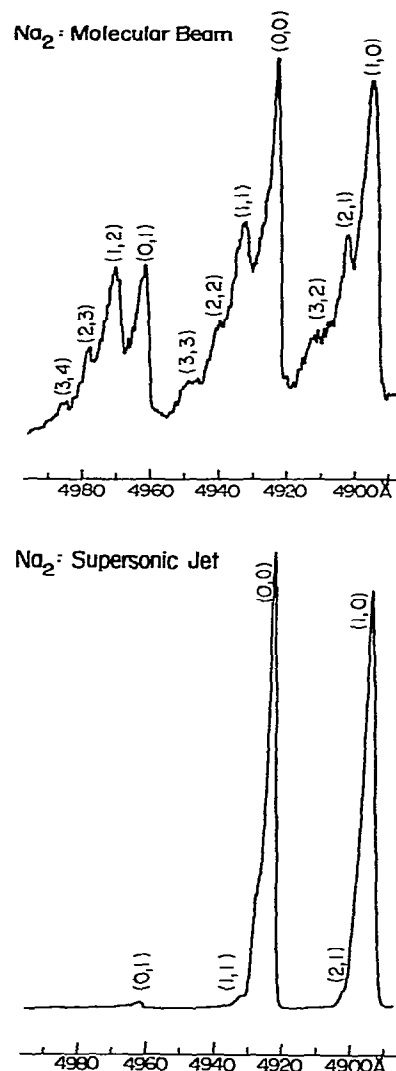


Fig. 1. Multiphoton ionization spectrum of Na_2 beam species. The ion signal is shown as a function of laser wavelength.

based on the fluorescence spectrum of Na_2 taken under similar conditions. They reported that the rotational temperature is about $55 \pm 10 \text{ K}$, while the vibrational temperature is $153 \pm 5 \text{ K}$. The apparent rotational temperature deduced from fig. 1 is warmer while the apparent vibrational temperature is colder. The former is due to a broadening of the bands in the MPI spectrum while the latter is due to the ratio of the signal strengths for the bands arising from the $v'' = 0$ and $v'' = 1$ levels.

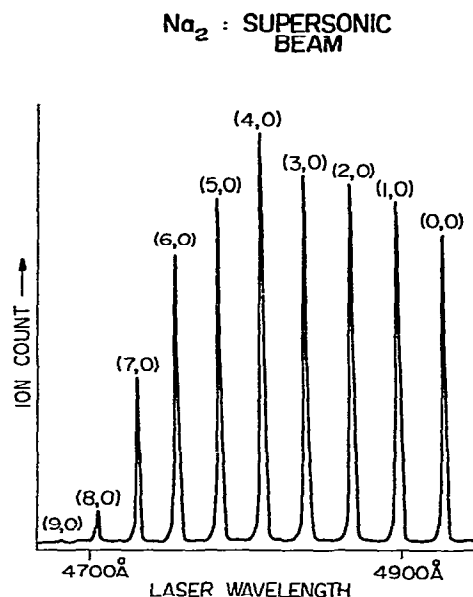


Fig. 2. The MPI spectrum of Na_2 molecules in a supersonic beam. The signal envelope follows the dye laser intensity (Exciton dye C481).

2.2. BaCl reaction products

The MPI technique can also be applied to detect the products of a beam-gas reaction, as illustrated here for the prototype system $\text{Ba} + \text{HCl}$ [16]. The apparatus used is the same as described previously [17] with the exception of the replacement of the photomultiplier tube with a 21 stage CuBe dynode multiplier and the addition of a 2" focal length lens to concentrate in the reaction zone the output of the pulsed dye laser.

An MPI spectrum generated under typical conditions (Ba flux $\approx 10^{15}$ atom $\text{cm}^{-2} \text{s}^{-1}$, HCl pressure $\approx 1 \times 10^{-4}$ torr) is shown in fig. 3 along with the laser-induced fluorescence (LIF) spectrum obtained under the same conditions. Apart from the very strong, sharp lines in the MPI spectrum, which are due to three-photon ionizations of Ba atoms [5], the major differences between the two spectra are the intensity ratios of the various Δv sequences and the lack of resolution of individual band heads in the MPI spectrum. The first effect is due mainly to the fact that these spectra are uncorrected for laser intensity, but intensity anomalies such as those found in the Na_2 spectrum must also be considered. This multiphoton process is more sensitive to variations in laser intensity than is fluores-

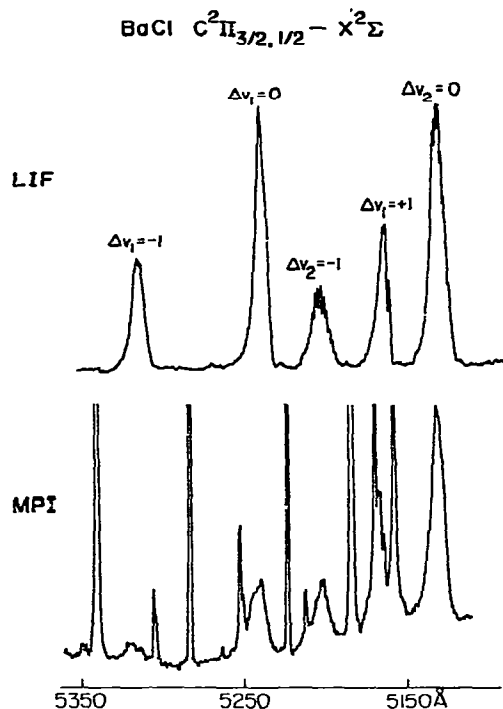


Fig. 3. Laser-induced fluorescence (LIF) and multiphoton ionization (MPI) spectra of BaCl produced in the beam-gas reaction $\text{Ba} + \text{HCl} \rightarrow \text{BaCl} + \text{H}$. The additional spectral features (many off-scale in signal intensity) found in the MPI spectrum are attributed to the multiphoton ionization of Ba. A subscript 1 or 2 on the Δv sequence denotes a transition involving ${}^2\Pi_{3/2}$ or ${}^2\Pi_{1/2}$, respectively.

cence, and the correction of the MPI spectrum is complicated by the dependence of the signal on the excitation intensity. A log-log plot of laser power versus the height of the $\text{C } {}^2\Pi_{3/2} - \text{X } {}^2\Sigma^+ \Delta v = 0$ peak is linear for an order of magnitude variation in laser intensity and gives a 1.4 power dependence for this two-photon process. A similar dependence cannot be assumed for the other Δv sequences. For example, measurements of the three-photon Ba ionization signals at 5535 Å ($6s^2 {}^1S_0 + h\nu \rightarrow 6s6p {}^1P_1^0 + 2h\nu \rightarrow \text{Ba}^+ + e^-$), at 5341 Å ($6s^2 {}^1S_0 + 2h\nu \rightarrow 6s7d {}^1D_2 + h\nu \rightarrow \text{Ba}^+ + e^-$), and at 5186 Å ($6s^2 {}^1S_0 + 2h\nu \rightarrow 6s8d {}^1D_2 + h\nu \rightarrow \text{Ba}^+ + e^-$) give power dependences of 2.2 ± 0.1 , 1.7 ± 0.1 , and 2.0 ± 0.1 , respectively.

We have also investigated the time evolution of the MPI signals shown in fig. 3. A difference of 0.5 μs was found for the arrival times of the signals due to the ionization of Ba and BaCl, under the experimental con-

ditions that the multiplier is ≈ 3 cm from the focal zone and is at a potential of 3000 V. The ratio of the square root of the total transit times corresponds well to the mass ratio of Ba^+ to BaCl^+ . This result shows that the multiphoton ionization of BaCl gives $\text{BaCl}^+ + e^-$ rather than $\text{Ba}^+ + \text{Cl}^-$, and suggests one potential advantage of MPI, namely, time-resolved mass spectrometry. For example, the MPI spectrum taken during the reaction of Ba with chlorobenzene under low temporal resolution is completely dominated by the atomic signal. With high temporal resolution, however, the signal due to BaCl clearly stands out from that due to Ba. Besides simplifying an overlapped, complicated spectrum, the exploitation of such time-of-flight differences could also be used to identify the species present.

3. Discussion

Although our preliminary results do not yet permit the relative population analysis desired for state-to-state studies of reaction dynamics, there are encouraging features. The signal-to-noise ratio in the MPI spectra of Na_2 and Ba is superior to that of the comparable LIF spectra. This results from a combination of factors. In Na_2 and Ba, there is a high probability for ion formation; every ion generated can be collected; and every collected ion can be counted. This should be contrasted with LIF detection in which it is practical to collect only a modest fraction of the emitted fluorescence, only part of which in turn can be counted because of the quantum efficiency (typically 20% at maximum) of photocathodes. Indeed, the high sensitivity of MPI is exemplified by the recently reported detection of single Cs atoms [7].

It is also instructive to examine potential sources of noise. In the LIF technique, the ultimate sensitivity appears often to be limited by scattered laser light, even with careful baffling. On the other hand, the MPI technique is unaffected by scattered light but is affected by an ion background, caused by irradiated surfaces, oven heaters, etc. However, this ion background is readily suppressed in practice. The ultimate sensitivity of the MPI technique presently appears to be limited more by fluctuations in the laser excitation source.

Multiphoton ionization as a detector of beam species and reaction products has additional advantages.

By using a visible laser, it is possible to detect species not having a visible absorption spectrum because of the multiphoton nature of this process. For example, the Ba Rydberg series was followed to its ionization limit (42032 cm^{-1}) and even beyond. We have already illustrated time-of-flight mass differentiation. It is a simple extension to carry out complete mass spectrometry by the insertion of a mass-selective element, such as a quadrupole mass filter, before the charged particle detector. Finally, it may be anticipated that MPI detection can be applied to systems where LIF detection is not practical.

The preliminary results presented here also point to several problems of the MPI detection technique. The MPI spectrum is broader than the LIF spectrum, and the relative intensities of the MPI spectral features are not readily related to laser intensity and to relative internal state populations. The lack of resolution in the MPI spectra indicates that the probability for ion formation is not so sharp a function of laser wavelength as that of fluorescence excitation. This may be caused by the efficiency of near-resonant multiphoton ionization and by the effects of the strong laser radiation field.

The theory for the intensity of the MPI signal is still in a state of development [18–21]. The dependence of the MPI signal on the laser intensity I , is not simply I^n , where n is the number of photons required for the ionization process. This phenomenon has been previously reported by others [3,4,7,8,11], and appears to be more the rule than the exception. In addition, we have observed here that the ion formation probability is not proportional to the Franck–Condon factor of the transition connecting the ground state and the real intermediate state. We propose a simple model that can account for both apparent anomalies. This model is based on consecutive absorption events, each of which has its own rate. In resonant multiphoton ionization, one rate will often dominate over the other. It is then the slowest rate process (the bottleneck step) that governs the overall rate of ion formation. For example, we interpret the MPI of Na_2 as being a rapid transition from the X to the B state followed by a slower transition from the B state to the ionization continuum. Then the ion signal has a pseudo-first-order dependence on the laser intensity and is independent of the B–X transition probability.

Similarly for Ba, our observations suggest that the

transition from the ground state $6s^2\ ^1S_0$ to the Rydberg level $6snd\ ^1D_2$ is the rate limiting step, causing the ion rate to show a pseudo-second-order dependence on the laser intensity. As expected, a more careful examination of our data shows deviations from a strict quadratic dependence which are outside of our error estimates. For BaCl, the rates for the consecutive absorption steps appear to be more nearly equal. This is seen in the dependence on laser intensity of $n = 1.4$ and the fact that the MPI spectrum resembles the LIF spectrum. As the theory for the relative MPI signal strength becomes better developed, it should be possible in some cases to extract information on the internal state distribution of the beam species by this technique, increasing significantly its potential utility.

Acknowledgement

We thank E. Schumacher and L. Wöste for stimulating discussions and for making available to us information on their work prior to publication.

References

- [1] R.N. Zare and P.J. Dagdigian, *Science* 185 (1974) 739.
- [2] J.L. Kinsey, *Ann. Rev. Phys. Chem.* Vol. 28 (1977), to be published.
- [3] B. Held, G. Mainfray, C. Manus, J. Morellec and F. Sanchez, *Phys. Letters* 35A (1971) 257; *Phys. Rev. Letters* 28 (1972) 130; 30 (1973) 423.
- [4] C.B. Collins, B.W. Johnson, D. Popescu, G. Musa, M.L. Pascal and I. Popescu, *Phys. Rev. A* 8 (1973) 2197; D. Popescu, C.B. Collins, B.W. Johnson and I. Popescu, *Phys. Rev. A* 9 (1974) 1182.
- [5] P. Esherick, J.A. Armstrong, R.W. Dreyfus and J.J. Wynne, *Phys. Rev. Letters* 36 (1976) 1296; J.A. Armstrong, P. Esherick and J.J. Wynne, *Phys. Rev. A* 15 (1977) 180; P. Esherick, *Phys. Rev. A* 15 (1977) 1920.
- [6] R.W. Solarz, C.A. May, L.R. Carlson, E.F. Worder, S.A. Johnson, J.A. Paisner and L.J. Radziemski, *Phys. Rev. A* 14 (1976) 1129.
- [7] J.S. Hurst, M.H. Nayfeh and P. Young, *Phys. Rev. Letters* 35 (1975) 1154; *Appl. Phys. Letters* 30 (1977) 229.
- [8] W.C. Lineberger and T.A. Patterson, *Chem. Phys. Letters* 13 (1972) 40.
- [9] P.M. Johnson, M.R. Berman and D. Zakheim, *J. Chem. Phys.* 62 (1975) 2500; P.M. Johnson, *J. Chem. Phys.* 64 (1976) 4143, 4638.
- [10] D.H. Parker, S.J. Sheng and M.A. El-Sayed, *J. Chem. Phys.* 65 (1976) 5534.
- [11] A. Herrmann, S. Leutwyler, E. Schumacher and L. Wöste, *Selective Absorption Spectroscopy of Clustered Alkali Beams*, VI International Symposium on Molecular Beams, Noordwijkerhout, The Netherlands, April 1977, post-deadline paper.
- [12] M.P. Sinha, A. Schultz and R.N. Zare, *J. Chem. Phys.* 58 (1973) 549.
- [13] R.D. Hudson, *J. Chem. Phys.* 43 (1965) 1790.
- [14] T.A. Patterson, H. Hotop, A. Kasdan, D.W. Norcross and W.C. Lineberger, *Phys. Rev. Letters* 32 (1974) 189.
- [15] W. Demtröder, M. McClintock and R.N. Zare, *J. Chem. Phys.* 51 (1969) 5495.
- [16] H.W. Cruse, P.J. Dagdigian and R.N. Zare, *Faraday Discussions Chem. Soc.* 55 (1973) 277.
- [17] P.J. Dagdigian, H.W. Cruse, A. Schultz and R.N. Zare, *J. Chem. Phys.* 61 (1974) 4450.
- [18] H.B. Bebb and A. Gold, *Phys. Rev.* 143 (1966) 143; H.B. Bebb, *Phys. Rev.* 149 (1966) 25.
- [19] G.S. Voronov, *Zh. Eksperim. i Teor. Fiz.* 51 (1976) 1496.
- [20] D. Grischkowsky, M.M.T. Loy and P.F. Liao, *Phys. Rev. A* 12 (1975) 2514.
- [21] P. Lambropoulos, *Advan. At. Mol. Phys.* 12 (1976) 87.