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Ahmed, Musahid

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Musahid Ahmed, Darcy S. Peterka, Paul Regan,
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Ion Pair Imaging Spectroscopy: $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3^+ + \text{Cl}^-$

Musahid Ahmed,^a Darcy S. Peterka,^a Paul Regan,^a
Xianghong Liu,^b and Arthur G. Suits^{b,c}

^aChemical Sciences Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, California 94720

^bChemistry Department
Brookhaven National Laboratory
Upton, New York 11973

^cDepartment of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794-3400

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Musahid Ahmed^a, Darcy S. Peterka^a, Paul Regan^a,
Xianghong Liu^b and Arthur G. Suits^{b,c,*}

^a*Chemical Sciences Division
Ernest Orlando Lawrence Berkeley National Laboratory
Berkeley, CA 94720*

^b*Chemistry Department
Brookhaven National Laboratory
Upton, NY 11973*

^c*Department of Chemistry
State University of New York at Stony Brook
Stony Brook, NY 11794-3400*

Abstract

The application of the velocity map imaging technique to study the vacuum ultraviolet photodissociation of molecules to give ion pair products can be a powerful means of probing ion energetics and spectroscopy. This approach, in many ways analogous to photoelectron spectroscopy, has the advantage that it may be applied to systems for which stable neutral precursors do not exist or may be difficult to prepare. In this Communication we describe the general technique and show the first demonstration of the method: $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3^+ + \text{Cl}^-$. The results provide insight into the vibrational frequencies of the methyl cation and the ion pair dissociation dynamics of methyl chloride, and illustrate some of the advantages of the method.

*arthur.suits@sunysb.edu

Photoelectron spectroscopy is an extremely powerful means of probing the energetics and vibrational frequencies of ionic species, and it has long been a principal source of insight into the electronic structure of molecules¹. Although it is a broadly used and nearly universal tool, there are a great number of systems of considerable importance for which photoelectron spectroscopy is simply not applicable owing to the absence of suitable neutral molecules as precursors or unfavorable Franck-Condon factors preventing access to the lowest levels of the ion. Even for direct probe techniques such as infrared absorption, the absence of convenient light sources at many wavelengths, unaccommodating selection rules and the challenge of generating ions under well-defined conditions often precludes general insight into the properties of important ions. As a result, there is little or no experimental data for many fundamental systems^{2,3}. The nonclassical carbonium ions, such as CH_5^+ and its homologues, are important examples. Even for the extensively studied and obviously important water cluster ions, i.e., H_5O_2^+ and related species⁴, infrared spectra outside the O-H stretching region are generally lacking, leaving fundamental structural questions still open.

A beautiful innovation in the study of ion energetics in recent years has been the development of Threshold Ion Pair Production Spectroscopy (TIPPS) by Martin and Hepburn^{5,6}. This approach is based upon the observation by Pratt and coworkers⁷ that long-lived ion pair states may be excited just below the dissociation threshold, then dissociated by application of a weak electric field following a brief delay. This provides extremely accurate determination of the energies of these dissociation limits in a process that is fully analogous to pulsed-field ionization or "zero electron kinetic energy" (ZEKE) photoelectron spectroscopy. Although this method affords unparalleled resolution for the determination of the thermochemistry of these dissociation thresholds, it is somewhat demanding in its requirements on the molecule, so that in practice it is not a very general technique. These requirements include 1) the existence of optically accessible Rydberg states that are effectively coupled to the ion-pair states at the energy of the dissociation limits, and 2) the absence of efficient alternative decay pathways such as predissociation or internal conversion that would prevent access to the ion pair states. Ion pair dissociation, nevertheless, provides an exciting opportunity to investigate the spectroscopy of some of the elusive ions mentioned above, if the TIPPS requirements can

be circumvented. Ion imaging, in particular the high resolution *velocity map imaging* variant that has emerged in recent years^{8,9}, represents precisely the means by which one can overcome these limitations and use ion pair dissociation as a general probe of some of these challenging systems, although not at the extraordinary level of resolution possible with TIPPS. This approach, which we term “Ion Pair Imaging Spectroscopy” (IPIS), is analogous to photoelectron imaging spectroscopy¹⁰, except the electron is replaced by an atomic anion. In this Communication, we outline the method, and provide a concrete example using results for ion pair imaging of CH₃Cl as a probe of the energetics of the methyl cation. Ion pair imaging was in fact first reported by Kawasaki and coworkers¹¹; their study predated the velocity map advance, however, so that the potential of the technique as a general probe of cation spectroscopy was not apparent in their work.

The technique is illustrated schematically in Figure 1 for the general case of ion pair dissociation of a stable precursor molecule, “MX” where X represents a halogen and M, in the case presented below, represents a methyl radical, but could be almost anything. Excitation, typically in the vacuum ultraviolet, leads to a Rydberg state that couples to the long-range ion-pair state. Dissociation of this state gives rise to momentum-matched X⁻ and M⁺ products, either of which may be detected using velocity map imaging. For the case of an atomic anion X⁻, the kinetic energy release, as manifested in the images, directly reflects the internal energy levels in the cation. In practice, the anion will generally give lower background and unambiguous indication of the ion pair process, while the cations are more likely to arise from other processes as well. On the other hand, the energies of the ion pair limits fall below the energy of direct ionization of the parent molecule owing to the sizable electron affinities of the halogen atoms, so that background interference from cations may actually be minimal. For the methyl chloride case, the kinematics were such that the results for the cation gave significantly higher resolution, and there was no evidence of background interference from other sources of CH₃⁺. In addition to ion pair imaging using stable precursor molecules, we envision two other alternatives directed to achieving insight into more exotic species; these are discussed below.

As a first example, we have applied the IPIS technique to probe the ion pair dissociation dynamics of methyl chloride at 118.3 nm and to gain insight into the vibrational frequencies of the methyl cation. A beam of methyl chloride seeded in H₂ (10%, 2 atm backing pressure) was expanded from a piezoelectric pulsed valve and skimmed once before entering a main chamber. There it interacted with a 118.3 nm VUV laser beam produced by frequency tripling the third harmonic of a Nd-YAG laser in xenon. The laser intersected the molecular beam at 45°. The laser polarization was linear, and parallel to the detector plane. The ions were extracted perpendicular to the beam plane, focused under velocity mapping conditions, directed through a field-free flight tube and projected onto an 80mm imaging detector. The detector was viewed by an integrating video system that accumulates images of the centroids of the ion spots as described above^{12,13}. Anion or cation images are readily obtained by reversing the voltages applied to the ion optics, and adjusting the detector potentials appropriately. The raw images clearly show that the limiting factor in determining the resolution is the velocity spread in the molecular beam. Accordingly, to obtain the highest resolution possible, we have “symmetrized” the images using just the quadrants of the image in which the recoil velocity is perpendicular to the molecular beam, so contribution of the longitudinal beam velocity spread in the final image is minimized. Future experiments will be done with the molecular beam directed into the detector, so that the longitudinal beam velocity spread will not contribute to the images at all.

An image of CH₃⁺ is shown in Figure 2. A series of rings are clearly in evidence, corresponding to vibrational excitations in the CH₃⁺. The images also show significant anisotropy indicating a prompt dissociation event and a parallel dissociation mechanism. Images for Cl⁻ give virtually identical results, albeit with lower resolution as mentioned above. Kawasaki and coworkers reported results for the same system (only for the cation), albeit using conventional ion imaging rather than velocity mapping. The broad features of our distributions agree, but there was no resolution of the underlying vibrational structure in the earlier work.

Analysis of the image is effected using established techniques: the inverse Abel transform is used to reconstruct the 3-D distribution, which is integrated to yield the translational energy distribution shown in Figure 3. These are shown along with combs

indicating calculated¹⁴ (harmonic) vibrational frequencies of CH_3^+ . Experimental values have been reported only for the ν_2 (umbrella)¹⁵ and ν_3 (C-H asymmetric stretch) modes^{16,17}, and the uncertainty in the former is considerable (see Table I). The anticipated dissociation dynamics accompanying a change in the methyl geometry from the near-tetrahedral of the parent molecule to the stiffly-planar methyl cation might lead one to predict considerable umbrella mode excitation in the CH_3^+ . This is apparently observed. In addition, peaks likely corresponding to combination bands with one quantum of ν_2 and one each of ν_1 or ν_3 are also seen. The relative vibrational populations extracted from the data are shown in Figure 4, obtained assuming the tentative assignments indicated in Figure 3. The umbrella mode excitation peaks at $v=2$, with considerable population in $v=3$ and 4 as well. The total C-H stretching excitation amounts to less than ten percent. In fact, we have neglected the ν_4 possibility; as can be seen from Table 1, the calculated ν_4 frequency is very close to ν_2 , but no experimental measurements are available. We see no reason in the dynamics to favor substantial ν_4 excitation, while there is the clear likelihood that the pyramidal-to-planar geometry change will lead to significant umbrella-mode excitation. We have thus assigned all of the excitation in that progression to ν_2 .

The peaks of the distributions are shifted somewhat from the predicted origins owing to possible uncertainties in the calculated vibrational frequencies, to instrumental blurring, and to the presence of rotational excitation in the CH_3^+ product. The latter will clearly represent one of the challenges of the IPIS method, and one way in which it is truly distinct from photoelectron spectroscopy: significant orbital angular momentum in the dissociation can allow for rotational excitation in the products to an extent not possible in photoelectron spectroscopy. The consequence, at least when the co-fragment is a relatively heavy atom, is that attention must be paid to the issue of rotational excitation when attempting to extract quantitative spectroscopic information from such data. The width of the peaks reflects both rotational excitation in the CH_3^+ , as well as broadening by instrumental factors. We have evaluated the contribution of the latter using a Monte Carlo image simulation program¹⁸ to investigate the nature of the broadening for different (infinitely sharp) recoil energies. The results are shown as dashed lines in Figure 5 for three different recoil energies. The broadening is almost

entirely a result of the velocity spread in the molecular beam, and this effect will be virtually eliminated in future experiments when the beam is directed into the detector (so that only the transverse beam velocity component contributes to the broadening.) As can be seen in the figure, the instrumental resolution is significantly worse for the higher energies; it is roughly constant in velocity space. Although it seems that velocity spread may account for some of the width of these peaks, it may not account for all of it, and rotational excitation may contribute as well. It should be straightforward to examine this in detail in future experiments.

We can make some assumptions to extract preliminary vibrational frequencies from the present data despite these complications. For the slowest-recoiling fragments, the rotational excitation must necessarily be small, so this interference will be minimal for these fragments. The peak associated with four quanta of umbrella-mode excitation contains very little translational energy, so that its associated rotational excitation must be negligible. Neglecting anharmonicity, we can use this peak to obtain the vibrational frequency of this mode. This approach yields the value 1370 cm^{-1} , which compares quite favorably with the calculated number as well as with the sole reported experimental value. For the combination bands, such a direct estimate is not possible owing to the fact that these peaks are associated with some kinetic energy and some possible rotational excitation. However, using simple estimates of this rotational excitation based upon the analogous pure umbrella-mode excitation peaks we obtain values of the vibrational frequencies shown in Table I. Although there is only one previously reported experimental value for the ν_3 frequency, it appears likely that the disagreement implies more rotational excitation present in these combination bands than in the nearby pure- ν_2 peaks. It should be emphasized, however, that this discussion rests upon a few assumptions that are admittedly questionable at this stage. Firstly, we have taken the thermochemistry from following sources: ΔH_f (0 K) of Cl and CH_3Cl , reference ¹⁹; ΔH_f (0 K), ionization energy of CH_3 , references ^{20, 21, 22}; electron affinity of Cl, reference ⁶. In fact, there is some disagreement ($\sim 300\text{ cm}^{-1}$) in the literature value for CH_3Cl ; indeed we may well be able to use the imaging technique to obtain a better value for this quantity. In addition, we assumed harmonic vibrational frequencies for

the v_2 progression, clearly a rough approximation. Finally this all relies on the assignments shown in Figure 3. Additional experiment and analysis will be necessary to address these questions unambiguously. It may well prove that an understanding of the dynamics of these processes is an important part of exploring their vibrational spectroscopy.

One alternative approach that may eliminate complications arising from rotational excitation is to use ion pair imaging of H^- rather than a halide ion. In this case the orbital angular momentum, hence the near-matching rotational excitation, will be much smaller. The large difference in the electron affinity means that this approach would require excitation deeper into the VUV, making it somewhat more challenging. Nevertheless, for some systems it may well prove an effective variation of the method.

In addition to ion pair imaging using stable precursor molecules, we envision two other variations on this technique directed to achieving insight into more exotic species. The first involves simply replacing the parent closed-shell molecule with a radical system. A concrete example closely related to the methyl chloride system is the chloromethyl radical. This can readily be produced by pyrolysis of bromo-chloromethane in a Chen-type pyrolytic pulsed valve²³. In this example, the ion pair formation threshold for CH_2Cl is 10.6 eV. This will allow direct probing of the vibrational frequencies of CH_2^+ , a fundamental system not readily accessible by other means. A second variant of the IPIS scheme relies on the use of appropriate precursor complexes to achieve a novel spectroscopic probe of some important ions mentioned above. In brief, a van der Waals complex $M..HCl$ (e.g. $CH_4..HCl$) is prepared in a molecular beam and excited by a VUV laser through the Rydberg states of HCl in the region from 8-11 eV. These states are strongly coupled to ion pair states $H^+ .. Cl^-$, so that decay to the ion pair channel is quite facile²⁴⁻²⁶. However, the ion pair threshold in free HCl is 14.4 eV, so that this decay path for HCl itself is not open; interference from ion pair or direct ionization processes involving free molecular species in the beam will thus be minimal. For the van der Waals complexes, however, the sizable proton affinity of the molecule M will draw this system to decay via the ion pair channel quite efficiently. As above, the imaging technique will be used to record the kinetic energy release in the Cl^- anion, directly mapping the internal energy in the corresponding cation. The thresholds for these

processes are roughly 10.4, 8.4 and 8.2 eV for H_3^+ , CH_5^+ and C_2H_7^+ , respectively, regions easily accessible using vacuum ultraviolet light produced by frequency mixing using conventional laser sources.

We have outlined a novel application of the velocity map imaging technique to obtain spectroscopic information on ionic systems not amenable to study using conventional techniques. We believe the approach to be quite general, and our preliminary results for the methyl chloride system show the promise of the technique as well as some of its challenges. Given the importance of many of these species, the scarcity of reliable spectroscopic information, and our preliminary successes with this approach, we believe it will be very rewarding to face these challenges.

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References

1. J. Berkowitz, *Photoabsorption, photoionization and photoelectron spectroscopy* (Academic Press, New York, 1979).
2. E. Hirota, *Chem. Rev.* **92**, 141 (1992).
3. E. Hirota, *Ann. Re. Prog. Chem. C* **96**, 95 (2000).
4. J. C. Jiang, Y. S. Wang, H. C. Chang, S. H. Lin, Y. T. Lee, and G. Niedner-Schatteburg, *J. Am. Chem. Soc.* **122**, 1398 (2000).
5. J. D. D. Martin and J. W. Hepburn, *Phys. Rev. Lett.* **79**, 3154 (1997).
6. J. D. D. Martin and J. W. Hepburn, *J. Chem. Phys.* **109**, 8139 (1998).
7. S. T. Pratt, E. F. McCormack, J. L. Dehmer, and P. M. Dehmer, *Phys. Rev. Lett.* **68**, 584 (1992).
8. M. V. Frohne, Ph. D., Kansas State, 1994.
9. A. Eppink and D. H. Parker, *Rev. Sci. Instrum.* **68**, 3477 (1997).
10. D. H. Parker and A. Eppink, *J. Chem. Phys.* **107**, 2357 (1997).
11. K. Suto, Y. Sato, C. L. Reed, V. Skorokhodov, Y. Matsumi, and M. Kawasaki, *J. Phys. Chem. A* **101**, 1222 (1997).
12. B. Y. Chang, R. C. Hoetzlein, J. A. Mueller, J. D. Geiser, and P. L. Houston, *Rev. Sci. Instrum.* **69**, 1665 (1998).
13. W. M. Jackson, D. Xu, R. J. Price, K. L. McNesby, and I. A. McLaren, in *Imaging in Chemical Dynamics*, edited by A. G. Suits and R. E. Continetti (American Chemical Society, Washington D. C., 2000), pp. 103.
14. R. V. Olkhov, S. A. Nizkorodov, and O. Dopfer, *J. Chem. Phys.* **108**, 10046 (1998).
15. J. Dyke, N. Jonathan, E. Lee, and A. Morris, *J. Chem. Soc., Faraday Trans. 2* **72**, 1385 (1976).
16. M. W. Crofton, W. A. Kreiner, M. F. Jagod, B. D. Rehfuss, and T. Oka, *J. Chem. Phys.* **83**, 3702 (1985).
17. M. W. Crofton, M. F. Jagod, B. D. Rehfuss, W. A. Kreiner, and T. Oka, *J. Chem. Phys.* **88**, 666 (1988).
18. L. S. Bontuyan, A. G. Suits, P. L. Houston, and B. J. Whitaker, *J. Phys. Chem.* **97**, 6342 (1993).

19. L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamics properties of individual substances* (Hemisphere, New York, 1989).
20. J. A. Blush, P. Chen, R. T. Wiedmann, and M. G. White, *J. Chem. Phys.* **98**, 3557 (1993).
21. M. Litorja and B. Ruscic, *J. Chem. Phys.* **107**, 9852 (1997).
22. B. Ruscic, M. Litorja, and R. L. Asher, *J. Phys. Chem. A* **103**, 8625 (1999).
23. H. Reisler, personal communication (2000).
24. E. F. van Dishoeck, M. C. van Hemert, and A. Dalgarno, *J. Chem. Phys.* **77**, 3693 (1982).
25. D. S. Green, G. A. Bickel, and S. C. Wallace, *J. Mol. Spectrosc.* **150**, 303 (1991).
26. D. S. Green and S. C. Wallace, *J. Chem. Phys.* **96**, 5857 (1992).

Table I. Comparison of calculated and experimental vibrational frequencies for CH_3^+ (in cm^{-1}).

Source	ν_1 (a_1')	ν_2 (a_2'')	ν_3 (e')	ν_4 (e')
MP2/aug-cc- pVTZ- $d(\text{H})$ - $f(\text{C})^a$	2912	1357	3108	1377
expt	-	1380(20) ^b	3108.4 ^c	-
IPIS (see text)	3117	1372	3387	-

^aReference 14.

^bReference 15.

^cReference 16,17.

Figure Captions

1. Schematic view of ion pair imaging spectroscopy technique.
2. Image of CH_3^+ from ion pair dissociation of methyl chloride at 118.3 nm. The laser polarization was vertical in the plane of the figure.
3. Total translational energy distribution for the ion pair process derived from the image in Figure 2, shown with vibrational frequencies calculated in reference 13. Dotted lines show estimated experimental resolution at 500, 2000 and 4000 cm^{-1} (see text).
4. Relative vibrational populations inferred from tentative assignments in Figure 3.

Fig 1
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Figure 2
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Figure 3
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Figure 4
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