MULTIPHOTON IONIZATION PHOTOELECTRON SPECTROSCOPY:
A NEW METHOD FOR DETERMINING VIBRATIONAL STRUCTURE OF MOLECULAR IONS

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By selecting various vibronic levels of the intermediate state in resonant two-photon ionization, different vibrational distributions are observed in the resulting photoelectron spectrum. In this manner additional vibrational information is obtained, compared to that found in one-photon VUV PES, including the observation of non-totally symmetric modes. This is illustrated for the chlorobenzene molecule.

1. Introduction

Photoelectron spectroscopy has been one of the most powerful methods for determining the electronic and vibrational structure of molecular ions [1]. For molecules with more than a few atoms however, it is sometimes very difficult to observe and interpret vibrational structure because of spectral congestion and because of the Franck—Condon principle which favors the appearance of only a limited number of vibrational modes. Multiphoton ionization (MPI) in conjunction with photoelectron spectroscopy (PES) has been used to help elucidate the multiphoton ionization mechanism [2–6], but has not really been applied to photoelectron spectroscopy problems until the work of Meek et al. [7] on toluene. In resonant two-photon ionization, a molecule can be excited through a number of real intermediate vibronic levels. Since each of these will have a different set of Franck—Condon factors and selection rules for ionization, we find that MPI photoelectron spectroscopy provides a means of obtaining additional vibrational information about polyatomic ions.

This new technique is illustrated on chlorobenzene (C_6H_5Cl) whose UV absorption spectrum has been well studied [8–10] and whose MPI spectrum is easily obtained [11,12]. By using different vibronic levels of the excited $^1B_2$ state, we are able to assign the vibrational frequencies of the first five in-plane modes of the chlorobenzene cation, identifying three modes which were previously unobserved.

2. Experimental

Photoelectron energy distributions were measured by a time-of-flight (TOF) method similar to that used by White et al. [13]. The TOF photoelectron energy analyzer used in these experiments is shown in fig. 1. It consists of a magnetically shielded flight tube, with an electrostatically shielded multichannel array electron detector (Galileo FTD2003) at one end, and an ionization source at the other. The ionizing laser (Quanta-Ray Nd : YAG pumped dye) is frequency doubled and the output focused into the TOF spectrometer with a cylindrical 150 mm focal length lens. The neutral molecules
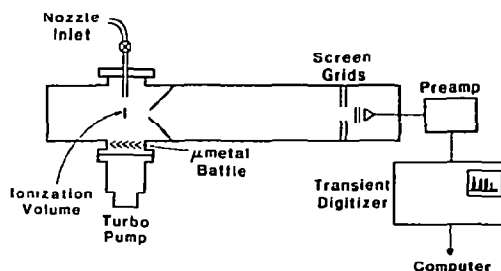

Fig 1. Schematic of experimental MPI PES apparatus.

are introduced into the ionization volume in a seeded ($\approx 1\%$ in argon) free-jet expansion, which serves to reduce hot-band congestion in the photoelectron spectra. The typical background pressure is 2×10^{-6} Torr.

Electrons are ejected from the ionization volume in all directions, and their kinetic energy distribution is measured by recording the electron arrival time distribution. Since no collection fields are used, only a small fraction ($\approx 5 \times 10^{-4}$) of the electrons are detected. In general, signal is not a problem, since in our rather large focal "stripe" we can produce up to $\approx 5 \times 10^4$ ions/shot before space-charge broadening of the electron energy distribution becomes apparent. Typical signal levels are 10 counts/shot By rotating the laser polarization vector, the photoelectron angular distribution is found to be anisotropic. The photoelectron signal for chlorobenzene is a factor of two greater when the polarization vector is along rather than perpendicular to the detection direction. The photoelectron spectra reported here were obtained by setting the linear polarization vector of the laser at the magic angle ($54.7°$) with respect to the detection direction.

Electron energy is inversely proportional to the square of the arrival time. The photoelectron spectrum is obtained by applying this transformation. The spectra are calibrated by measuring photoelectron spectra of xenon. Calibration is found to be stable to within 5% over a period of days.

3. Results and discussion

We ionize chlorobenzene by pumping with one photon to the first excited singlet state ($^1B_2$) of the neutral. On more photon of the same wavelength will then ionize the molecule. Fig. 2 shows the wavelength dependence of the ionization signal in the region just above the $^1B_2$ 0–0 band. The spectrum was taken in our TOF mass spectrometer and will be discussed in a later paper [12]. There are some questions remaining about the vibrational structure of the chlorobenzene molecule. Tentatively, we are using the vibrational state assignments and notation taken from the absorption spectroscopy work of Bist and co-workers [10].

Fig. 3 shows the photoelectron kinetic energy spectra taken at wavelengths pumping the first four vibrational levels of $^1B_2$ chlorobenzene. In fig. 3a ($\lambda_{ex} = 269.9$ nm), ionization occurs through the vibrationless level of the $^1B_2$ state Ions are formed almost exclusively in the ground vibrational state, with a small hot band observable to higher energies and a small shoulder appearing to the low-energy side of the main peak due to vibrationally excited ions In fig. 3b ($\lambda_{ex} = 267.78$ nm; $18b_0^1$), the resonant intermediate state has one quantum of ν_{18b} excited Ionization results in a distribution of vibrational excitation. The largest group of ions is formed with one quantum of ν_{18b} and smaller fractions appear with excitation of ν_{6b}, $\nu_{6b} + \nu_{18b}$, and in the vibrationless state. In fig. 3c ($\lambda_{ex} = 267.18$ nm; $6a_0^1$), ionization occurs through the ν_{6a} level of the $^1B_2$
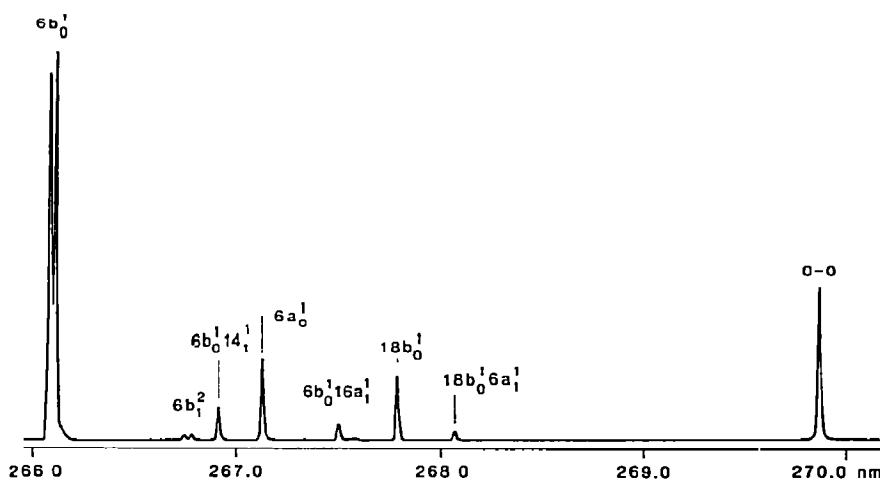

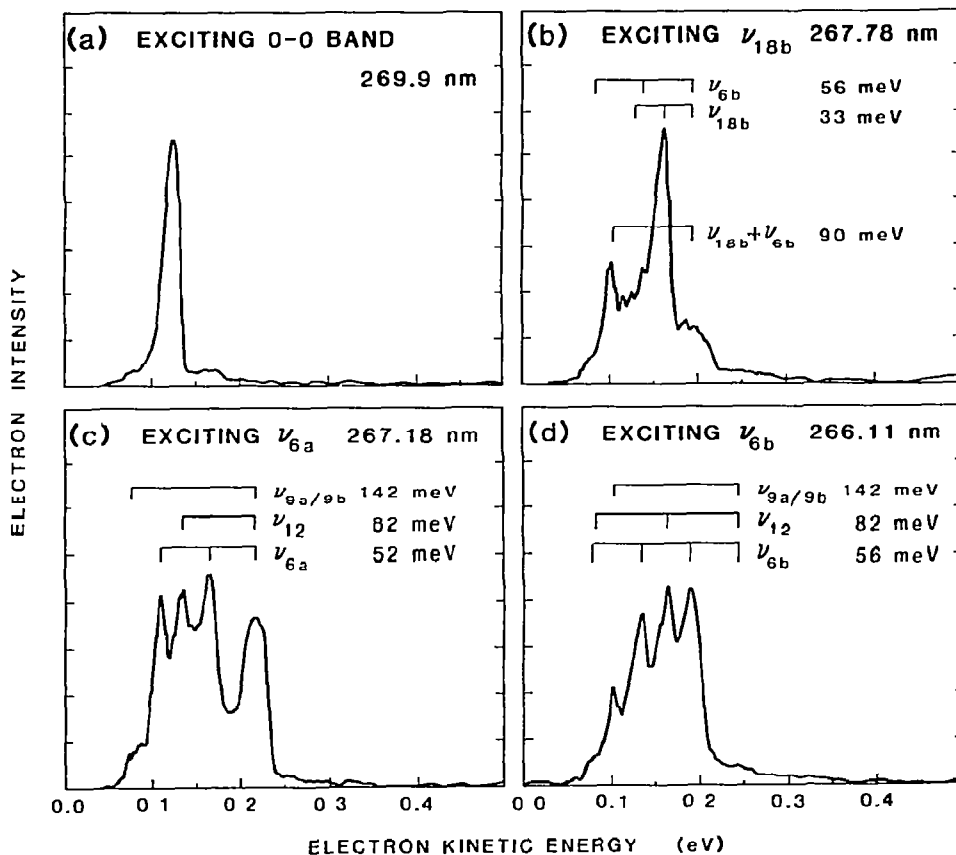Fig. 2. MPI spectrum of jet-cooled chlorobenzene showing parent ion signal versus wavelength.

Fig. 3. MPI PES spectra of chlorobenzene. Vibrational progressions and energy spacings are listed

state. The most prominent feature of the ion vibrational distribution is a progression in ν_{6a}. In addition, a substantial number of ions are formed with one quantum of ν_{12} and in a mode with a 142 meV frequency, which is possibly either ν_{9a} or ν_{9b} (denoted as $\nu_{9a/9b}$). In fig. 3d ($\lambda_{ex} = 266.12$ nm, $6b_0^1$), excitation is through ν_{6b} in the $^1B_2$ state. A short progression in ν_{6b} is observed in the ion as well as excitation of ν_{12} and $\nu_{9a/9b}$. Almost no ions are formed in the vibrational ground state. The measured ion vibrational frequencies are summarized in table 1 along with the corresponding ground-state and excited-state ($^1B_2$) frequencies of the neutral.

Finally we note that no electrons (±3% of total signal) are observed with kinetic energies greater than expected from ionization at the two-photon level of excitation. This is true not only under the low power density con-

ditions used in taking the reported spectra ($\approx 1 \times 10^7$ W/cm^2), but also when using the focused 4th harmonic of the Nd . YAG laser ($\approx 1 \times 10^9$ W/cm^2). Similar results were obtained for benzene by Meek et al. [3].

Clearly, by changing the intermediate vibronic level in resonant two-photon ionization, we are able to alter the ion vibrational distribution. Single-photon VUV photoelectron spectroscopy usually involves an electronically allowed transition from a bound orbital to an outgoing wave. As such, vibronic interactions play a minor role except where there are Jahn–Teller effects [1]. The consequence of this is that totally symmetric (a_1) vibrational modes predominate in the photoelectron spectra [14]. In MPI PES, the use of an intermediate *vibronic* level permits non-totally symmetric vibrations (in this case, b_2) to appear in the final ion

Table 1
Comparison of the measured vibrational frequencies in the chlorobenzene cation to those of the neutral ground state and $^1B_2$ excited state

Vibrational mode (C_{2v} symmetry)	Neutral ground state ($^1A_1$), ref. [10] (cm^{-1})	Neutral excited state ($^1B_2$), ref. [10] (cm^{-1})	Ion ground state ($^2B_1$), present work (cm^{-1})
18b (b_2)	294.7	287.3	266 ± 15
6a (a_1)	416 8	378.2	419 ± 10
6b (b_2)	614.9	521.0	451 ± 10
12 (a_1)	706 5	671.3	661 ± 10
9a (a_1)	1153.0	980.6 ⎱	1145 ± 15 [a]
9b (b_2)	1167 1	1149 4 ⎰	

[a] Assignment unclear.

state distribution. Moreover, by tuning to different vibronic levels of the intermediate, one has some control over the nature of the final-state vibrational modes. To the extent that the intermediate state has a geometry similar to that of the ion, excitation through a particular vibronic level of the intermediate tends to result in the appearance in the ion of a short progression in the same vibrational mode and the excitation of only a few other vibrational modes Several advantages appear to accrue from the ability to "tune" the product of the vibronic selection rules and Franck–Condon factors for each single-photon transition. Assignment of the spectra is greatly simplified. This helps to overcome a major problem confronted in many single-photon PES studies where the vibrational assignments are often best educated guesses. In addition, spectral congestion is reduced, since different ion vibrational modes appear when ionization is through different intermediate vibronic levels. For example, the frequencies of ν_{6a} and ν_{6b} are easily measured in spite of the fact that the difference in their frequencies (4 meV) is smaller than our instrumental resolution. Finally, we stress that the frequencies of non-totally symmetric ion vibrational modes may be determined

4. Conclusion

MPI photoelectron spectra of chlorobenzene have been presented. We have measured the frequencies of five vibrational modes of the chlorobenzene cation, in-

cluding two non-totally symmetric modes which are not observed in the conventional single-photon PES [14]. When these results are examined together with those of Meek et al. [7] on toluene, it is apparent that MPI PES should provide a powerful, general method for determining the vibrational structure of ground-state molecular ions.

Acknowledgement

References

[1] D.W. Turner, C. Baker, A.D. Baker and C.R. Brundle, Molecular photoelectron spectroscopy (Wiley, New York, 1970);
K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S -E. Karlsson, I. Lindgren and B. Lindgren, ESCA- Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy, Nova Acta Regiae Societatus Scientiarum Upsaliensis, Ser. IV, Vol. 20 (1967);
J.W. Rabalais, Principles of ultraviolet photoelectron spectroscopy (Wiley, New York, 1977).

[2] R.N. Compton, J.C. Miller, A.E. Carter and P. Kruit, Chem
Phys Letters 71 (1980) 87;
J C. Miller and R.N. Compton, J. Chem Phys. 75 (1981)
22, 2020.

[3] J.T. Meek, R.K Jones and J.P. Reilly, J. Chem. Phys 73
(1980) 3503.

[4] J. Kimman, P. Kruit and M.J. van der Wiel, Chem Phys
Letters 88 (1982) 576.

[5] G.J. Fisanick, A. Gedanken, T S Eichelberger IV,
N.A. Kuebler and M B Robin, J. Chem. Phys. 75
(1981) 5215.

[6] Y. Achiba, K Sato, K Shobatake and K Kimura,
J. Chem. Phys. 77 (1982) 2709.

[7] J T Meek, S.R Long and J P. Reilly, J. Phys. Chem.
86 (1982) 2809.

[8] H. Sponer and S.H Wollman, J. Chem. Phys 9 (1941)
816.

[9] T. Cvitaš and J.M. Hollas, Mol Phys. 18 (1970) 101.

[10] H D. Bist, V N Sarin, A Ojha and Y.S. Jain, Appl.
Spectry 24 (1970) 292;
Y.S. Jain and H.D. Bist, J Mol Spectry. 47 (1973) 126.

[11] J. Murakami, K Kaya and H. Ito, J. Chem. Phys. 72
(1980) 3363.

[12] D M. Rider, J Durant, S L Anderson, D. Proch and
R N. Zare, to be published.

[13] M G. White, R A. Rosenberg, G Gabor, E.D Poliakoff,
G. Thornton, S.H. Southworth and D.A. Shirley, Rev.
Sci Instr 50 (1979) 1268.

[14] I. Reineck, R. Maripuu, C. Nohre, P. Lodin, L Karlsson
and K. Siegbahn, to be published