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COMMUNICATIONS

Vibrational state dependence of ionic rotational branching ratios in resonance enhanced multiphoton ionization of CH

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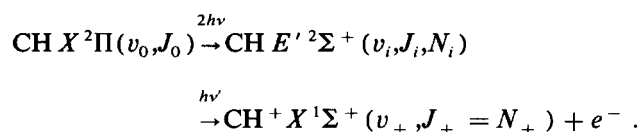
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Combined with high-resolution photoelectron spectroscopy, resonance enhanced multiphoton ionization (REMPI) is an important probe of the photoionization dynamics of excited molecular states at a quantum-state-specific level.¹⁻³ Whereas much interest has been focused on vibrationally resolved REMPI spectra and the insight such spectra provide on the resonant and ionized state dynamics, rotationally resolved spectra not only extend our understanding of the underlying ionization dynamics but also obviously play a role in the use of this technique for state-specific production of ions.⁴⁻⁶ Among small molecules, the REMPI spectra of diatomic hydrides such as CH, NH, and OH are of particular interest because of their importance as dissociation fragments and reactive intermediate species. The Rydberg states of diatomic hydrides share a common, rather simple, electronic structure: the first Rydberg state is repulsive (σ -type Rydberg orbitals consist mainly of a mixture between $3s_A$ and antibonding $2p_{zA}-1s_B$ orbitals), followed by a set of Rydberg states whose potential energy curves closely resemble that of the associated ion.⁷ Recently, we have shown that rapid evolution of the Rydberg orbital with internuclear distance (further enhanced by the presence of a Cooper minimum) can lead to strong non-Franck-Condon effects in ion vibrational branching ratios measured in REMPI, as predicted for OH and other diatomic hydrides.⁸

The purpose of this Communication is to illustrate the striking and significant influence this rapid orbital evolution of the resonant Rydberg state has on the ionic rotational distributions as the level of vibrational excitation in the resonant state increases. As a specific example of this effect we present results of *ab initio* calculations of these branching ratios for $(2 + 1')$ REMPI of CH via the $E' \ ^2\Sigma^+(3p\sigma)$ state. This is similar to the excitation scheme used in the recent work by Chen *et al.*⁹ in which the E' state was probed by REMPI for the first time:



Here we choose excitation via the $O_{11}(20.5)$ branch, i.e., $J_0 = 20.5$, $J_i = 18.5$, and $N_i = 18$. For a $\Sigma-\Sigma$ transition as in the photoionization step of the above reaction, a $\Delta N + l = \text{odd}$ selection rule applies,¹⁰ where ΔN is the change of the rotational quantum number (excluding spin) between the intermediate and final state, and l denotes a partial-wave component of the photoelectron orbital. For the $E' \ ^2\Sigma^+(3p\sigma)$ state of CH, this selection rule therefore predicts a $\Delta N = \text{odd}$ propensity rule, since an atomic photoionization picture would predict dominance of even partial waves in the photoelectron orbital (i.e., $3p \rightarrow ks, kd, \dots$).

The electronic wave function for the $E' \ ^2\Sigma^+(3p\sigma)$ state of CH (with the dominant configuration¹¹ $1\sigma^2 2\sigma^2 3\sigma^2 5\sigma$) was determined using the improved virtual orbital method¹² with the CH^+ orbitals for the core. The continuum photoelectron orbitals were obtained using the iterative Schwinger method.¹³ The explicit R dependence of the transition moment between the initial state $|i\rangle$ and the final state $|f\rangle$ was included via the transition moment $\int dR \chi_f^*(R) r_{fi}(R) \chi_i(R)$, where $r_{fi}(R)$ is the bound-free electronic transition moment at an internuclear distance R . The electronic wave functions and transition moments were calculated over a range of internuclear distances from $R = 1.6 a_0$ to $R = 3.2 a_0$, and the vibrational wave functions χ_f and χ_i were obtained numerically using the potential curves calculated by van Dishoeck¹¹ for the $E' \ ^2\Sigma^+$ state, and by Green *et al.*¹⁴ for the $X \ ^1\Sigma^+$ state of CH^+ . The coupling between partial waves of the continuum orbital and the molecular rotation was treated explicitly, employing a method previously described.⁴⁻⁶ Both the intermediate state and the final state were treated in Hund's case (b) coupling

scheme.¹⁵ Further details of the calculations will be reported in a separate paper.

The evolution of the 5σ orbital of the $E'^2\Sigma^+$ state is very rapid as a function of internuclear distance: it changes from predominantly $3p$ character at small internuclear distances to predominantly $3s$ character at larger internuclear distances. A single-center expansion of the 5σ orbital around the center-of-mass yields a 14.8% s , 84.7% p , and 0.5% d character at $R = 1.6 a_0$, and a 81.6% s , 5.3% p , and 10.6% d character at $R = 3.2 a_0$. This orbital evolution is similar to that for the $D^2\Sigma^-(3p\sigma)$ state of OH,⁸ and in the present case also leads to strong non-Franck-Condon behavior in ion vibrational branching ratios (not shown). This orbital evolution also results in a dramatic dependence of the partial-wave composition of the transition moment as a function of internuclear distance. An atomic photoionization picture would therefore predict, as a function of internuclear distance, the even l partial waves (s, d, \dots) to be dominant at small internuclear distances and the odd partial waves (p, f, \dots) at larger internuclear distances.

In Fig. 1 we show calculated ionic rotational branching ratios for the $O_{11}(20.5)$ branch via the $E'^2\Sigma^+$ state of CH, for the $v_i = 0-3$ vibrational levels of the resonant intermediate state. The branching ratios have been convoluted with a Gaussian detector function with a full width at half-maxi-

mum (FWHM) of 6 meV. Only the diagonal ($\Delta v = v_+ - v_i = 0$) vibrational branches are presented since these are predicted to have the strongest signals, as expected on basis of the Rydberg nature of the E' state. The ionic rotational branching ratios are determined for the $O_{11}(20.5)$ branch because it is a "clean" branch, and it has reached the high- J limit, where the rotational branching ratios are symmetric around $\Delta N = 0$. Since $N_i = 18$, the $\Delta N = 0$ peak corresponds to $N_+ = 18$. The rotational branching ratios are seen to be very dependent on the vibrational level accessed in the intermediate state, with a strong $\Delta N = \text{odd}$ (i.e., $l = \text{even}$) propensity rule apparent in lower vibrational levels and a $\Delta N = \text{even}$ (i.e., $l = \text{odd}$) propensity rule for higher vibrational excitation. This vibrational dependence of the propensity rule is caused by the extended portion of the potential well sampled by the higher vibrational levels, i.e., the region of R where the Rydberg orbital itself has evolved from $3p\sigma$ to mainly $3s\sigma$ type. The photoelectron kinetic energy is kept constant (100 meV in the present calculations). The branching ratios are somewhat (but not strongly) dependent on the final kinetic energy, and results indicate (not shown) that this effect remains very pronounced at higher kinetic energies. In conclusion, we point out that this vibrational dependence of the ionic rotational propensity rule should be quite general, and is expected to

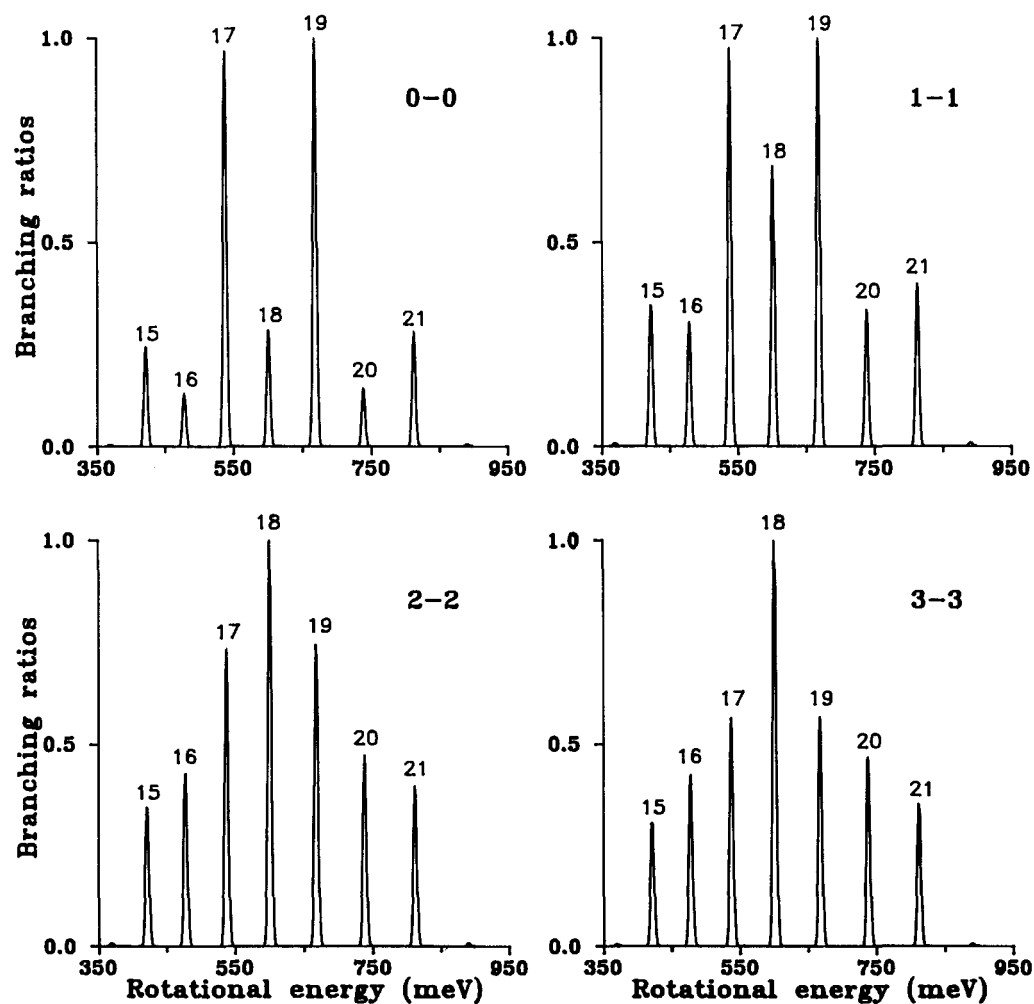


FIG. 1. Ionic rotational branching ratios for $(2+1')$ REMPI via the $O_{11}(20.5)$ branch of the $E'^2\Sigma^+(3p\sigma)$ state of CH for various vibrational levels of the E' state. The value of v_i and v_+ is indicated ($\Delta v = 0$) in the upper right corner of each frame. The value of N_+ is indicated over each photoelectron peak. The photoelectron kinetic energy is 100 meV.

occur in the other diatomic hydrides in which the Rydberg orbital of the resonant intermediate state exhibits rapid evolution with internuclear distance. The hydrides are particularly suitable for ionic rotationally resolved experiments, since the large rotational constant of the ion makes the required rotational resolution feasible at lower N_+ levels.

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⁷H. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, Orlando, 1986), Chap. 4, Sec. 2. Rydberg states may deviate considerably from their associated ion under conditions of strong Rydberg–valence mixing. The present discussion pertains to Rydberg states which are well described by a single electronic configuration, over a range of internuclear distance typically spanning several lower vibrational levels.

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NOTES

Ab initio molecular orbital study on the methylation affinity of N₂

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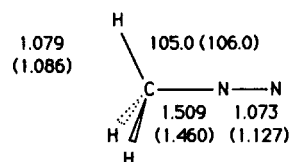
The purpose of this note is to present calculated results on the methylation affinity of N₂.

Recently McMahon *et al.*¹ reported the methylation affinity ladder of various compounds, where the absolute value of N₂ estimated through the experimental heat of formations^{2–4} of CH₃N₂⁺ and CH₃⁺ was used as a primary standard. They pointed out that the detailed computations on an absolute methylation affinity should be very desirable.

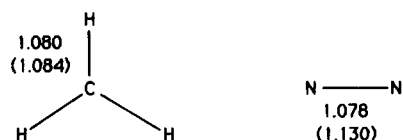
Although there are a few papers^{5–7} which theoretically discussed the geometry of CH₃N₂⁺ and the energy change in reaction (1), their methods and basis sets are not enough to discuss the absolute thermochemical data of the reaction



Completely optimized geometry of CH₃N₂⁺ and its frequencies are shown in Fig. 1; the data on CH₃⁺ and N₂ are also shown. The geometries optimized by the second-order Møller–Plesset perturbation method (MP2)^{8,9} were used for further energy calculations. Table I lists the total energies



346(e), 769, 1167(e), 1436, 1496(e), 2221
3147, 3289(e) cm⁻¹



1473, 1484(e), 3156, 3375(e) cm⁻¹ 2180 cm⁻¹

FIG. 1. HF and MP2 geometries optimized with the 6-31G(d,p) basis set; the values in the parentheses indicate the MP2 ones. The bond lengths in angstrom and the angles in degree. MP2 frequencies (in cm⁻¹) are also listed (no factors were multiplied).