

Rovibrational-State-Selected Photoionization of Acetylene by the Two-Color IR + VUV Scheme: Observation of Rotationally Resolved Rydberg Transitions

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We have demonstrated a rovibrational-state-selected photoionization experiment using an IR laser and high-resolution VUV-synchrotron radiation. The VUV photoionization of acetylene [$C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1, J' = 8 \text{ or } 10)$] prepared by IR excitation reveals three strong autoionizing Rydberg series converging to $C_2H_2^+(\tilde{X}^2\Pi_u; \nu_3^+ = 1)$ with little ion background interference. Rotational transitions resolved for the Rydberg states provide an estimate of ≈ 1.8 ps for their lifetimes. This experiment opens the way for state-selective photoionization studies of polyatomic molecules using VUV-synchrotron radiation.

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The vibrational modes of a polyatomic ion that can be excited in photoionization are governed by symmetry selection rules and Franck-Condon factors (FCFs) in the ionization transitions [1,2]. Since photoionization usually begins with a molecule in its ground vibrational state, the intensity of an excited ion vibrational band observed in the photoelectron spectrum is proportional to the FCF between the ground state of the neutral and the excited vibrational state of the ion. The value for such an FCF connecting to an excited ion vibrational state is appreciable when the bonding between the atoms associated with this vibrational mode is strongly perturbed by the ejection of a photoelectron. On the contrary, the FCF associated with an excited ion vibrational state is negligibly small if the removal of the photoelectron has little effect on the bonding property of the atoms comprising the vibrational motion. As such, ion vibrational modes belonging to the latter category cannot be excited by direct single-photon ionization that usually occurs in the vacuum ultraviolet (VUV). However, these ion vibrational modes may be examined by employing a two-color infrared (IR)-VUV photoionization scheme. By first preparing the neutral molecule in a selected vibrational state using an IR laser, it is plausible that the subsequent VUV-photoionization transition is shifted to a region of phase space, giving rise to a larger FCF for the formation of the excited ion vibrational state of interest. Furthermore, the two-color IR-VUV scheme is governed by optical selection rules different from those for single-photon photoionization. Thus, autoionizing Rydberg states and ion vibrational states that cannot be examined by single-photon photoionization may be studied by the IR-VUV photoionization method. An important application of photoionization measurements is an accurate determination of ionization energies (IEs) of molecules [3]. The hot-band effect, due to thermal excitation of rotational and low frequency vibrational modes, is known to complicate and limit the precision of IE values of polyatomic mole-

cules obtainable in photoionization measurements [3]. The preparation of the molecule in a single rovibrational state by IR excitation prior to VUV photoionization will eliminate the hot-band problem in IE measurements. In addition, when the geometries of the neutral molecule and its ion involved in a photoionization process are very different, the FCF for producing the ground state ion can be negligibly small, making it difficult to obtain a reliable IE value from the photoion spectrum [3]. Such a problem may also be alleviated using the IR-VUV photoionization scheme. By preparing the neutral molecule in an appropriate vibrational state, the FCF for forming the ion in its ground state can be increased, thus enhancing the sensitivity in IE determinations.

Elegant double-resonance photoionization studies [4–6] involving IR excitation and UV photoionization have been reported previously. These experiments have provided a wealth of information on state-selective photoionization of molecules. However, the UV photoionization in these experiments was accomplished by the absorption of two UV photons involving a 1 + 1 resonance-enhanced photoionization mechanism. Because of the mediation of the intermediate electronically excited level, the nature of these IR-UV photoionization studies is different from that of an IR-VUV photoionization experiment. Furthermore, since a well-characterized, long-lived electronically excited state is required in the IR-UV photoionization process and such an excited state may not exist for the molecule of interest, the IR-UV photoionization scheme can be applied only to selected molecules. The fact that the IR-VUV photoionization scheme does not require an intermediate state makes it a general scheme, applicable to all polyatomic molecular species.

In this Letter we report the demonstration of a rovibrational-state-selected photoionization experiment on acetylene (C_2H_2) by employing the IR-VUV scheme. Neutral $C_2H_2(\tilde{X}^1\Sigma_g^+)$ has five vibrational modes [7–9],

ν_1 (symmetric C-H stretching), ν_2 (symmetric C-C stretching), ν_3 (antisymmetric C-H stretching), ν_4 (degenerate symmetric bending), and ν_5 (degenerate antisymmetric bending). The degeneracy for the bending modes is removed in $C_2H_2^+(\tilde{X}^2\Pi_u)$ by Renner-Teller interactions [10], giving rise to seven vibrational modes. The formation of $C_2H_2^+(\tilde{X}^2\Pi_u)$ results from the removal of an electron from the π -bonding orbital of C_2H_2 . This has the effect of weakening the C-C bond, as manifested in the lowering of the ν_2^+ (symmetric C-C stretching) ion frequency by $\approx 8\%$ with respect to the ν_2 frequency [7–11]. Although the frequencies for the C-H stretching modes, ν_1^+ (symmetric stretch) and ν_3^+ (antisymmetric stretch), are also slightly lowered compared to the corresponding neutral vibrational frequencies [7–11], the removal of a π -bonding electron has only a minor effect on the C-H bond. Consistent with this expectation, the photoelectron spectrum for C_2H_2 was found to exhibit the ν_2^+ vibrational progression along with combination vibrational bands consisting of ν_2^+ and the bending vibrations for $C_2H_2^+(\tilde{X}^2\Pi_u)$ [10,12]. Excited vibrational bands for the C-H stretching modes (ν_1^+ and ν_3^+) of the $C_2H_2^+(\tilde{X}^2\Pi_u)$ ion by direct photoionization of C_2H_2 have not been observed in single-photon photoelectron measurements, although excitation of the ν_1^+ mode is known to occur via autoionization [13]. We have performed an FCF calculation [2,14] for the photoionization transition $C_2H_2^+(\tilde{X}^2\Pi_u) \leftarrow C_2H_2(\tilde{X}^1\Sigma_g^+)$. This calculation is in qualitative accord with previous experimental observations, indicating no excitation of the C-H vibrational modes of the ion. The ν_3 mode has σ_u symmetry and can readily be excited by an IR laser. The subsequent VUV photoionization of $C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1)$ thus prepared is expected to produce $C_2H_2^+(\tilde{X}^2\Pi_u; \nu_3^+ = 1)$ with the highest intensity compared with those for other excited vibrational modes. This expectation is also confirmed by the FCF calculation [2,14], which predicts that the lowest energy and strongest vibrational band to be observed from the direct photoionization of $C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1)$ is that of the $C_2H_2^+(\tilde{X}^2\Pi_u; \nu_3^+ = 1)$ state at 3136 cm^{-1} above the $IE[C_2H_2(\tilde{X}^1\Sigma_g^+)]$ [7,10,11,15]. All other vibrational bands at energies up to 6600 cm^{-1} above the $IE[C_2H_2(\tilde{X}^1\Sigma_g^+)]$ are predicted to be combination bands involving ν_3^+ and to be substantially weaker than that for the ν_3^+ mode. Based on the continuity of oscillator strength density, we expect to observe strong autoionizing Rydberg states converging to the $C_2H_2^+(\tilde{X}^2\Pi_u; \nu_3^+ = 1)$ in the region of $0\text{--}3136\text{ cm}^{-1}$ above the $IE[C_2H_2(\tilde{X}^1\Sigma_g^+)]$. Autoionizing Rydberg states converging to the $C_2H_2^+(\tilde{X}^2\Pi_u; \nu_2^+ = 1, 2)$ states were observed in previous single-photon VUV-photoionization studies [16]. Those autoionizing Rydberg states are superimposed on a strong $C_2H_2^+$ continuum produced by direct photoionization, complicating the analysis of the autoionizing structures. In contrast, since the FCF is zero for the formation of the ground ionic state $C_2H_2^+(\tilde{X}^2\Pi_u)$ from $C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1)$, ions will

be generated only from the autoionization of the Rydberg states converging to $C_2H_2^+(\tilde{X}^2\Pi_u; \nu_3^+ = 1)$. The ion signal is expected in principle to have a zero contribution by direct photoionization if the VUV energy is below the $IE[C_2H_2(\tilde{X}^1\Sigma_g^+)]$. Taking into account the IR frequency of 3289 cm^{-1} , the VUV-frequency range of interest in the present experiment is $88\,560\text{--}91\,544\text{ cm}^{-1}$, i.e., $412\text{--}3396\text{ cm}^{-1}$ below the $IE[C_2H_2(\tilde{X}^1\Sigma_g^+)] = 91\,956 \pm 1\text{ cm}^{-1}$ [15]. Hence, only thermally excited C_2H_2 can form ions by single-photon photoionization. At room temperature these ions do not contribute a significant background in the present experiment. To the best of our knowledge, the high-lying Rydberg states converging to $C_2H_2^+(\tilde{X}^2\Pi_u; \nu_3^+ = 1)$ have not been observed previously.

The experimental arrangement is similar to that described in detail in a recent report [17] on the VUV-IR (VUV excitation followed by IR photoionization) photoionization study of Ar. A high-repetition rate (3.7 kHz) IR optical parametric oscillator (OPO) [18] resonating in the idler wavelength and the high-resolution VUV-synchrotron source (tunable range = $8\text{--}25\text{ eV}$) at the Chemical Dynamics Beamline of the Advanced Light Source (ALS) [19] were used as the light sources. The major advantage of these light sources is their ease of tunability as well as their broad tunable photon energy ranges. The relatively long radiative lifetime of vibrationally excited species is also a favorable feature in the present experiment. This feature alleviates the mismatch in repetition rates of the IR-OPO and the VUV-synchrotron source so that temporal synchronization is not critical.

Acetylene is introduced into the photoionization region as an effusive beam with an estimated C_2H_2 pressure of $\approx 1 \times 10^{-3}$ Torr at the photoionization region. Optimal spatial overlap of the invisible IR and VUV beams is established by the Ar^+ signal formed by two-color VUV-IR photoionization [17]. The IR-OPO is tuned to prepare a well-defined initial rotational level J' (8 or 10) of $C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1)$. The photoion spectra for $C_2H_2^+$ are obtained by scanning the VUV-synchrotron source in an energy step of 0.3 or 1.0 meV. In order to correct for the background ion contribution due to direct VUV photoionization of thermally excited C_2H_2 , all photoion data presented here have been obtained by taking the difference between the ion counts observed with the IR beam on and off.

Figure 1(a) shows the photoion spectra for $C_2H_2^+$ in the VUV range of $10.97\text{--}11.35\text{ eV}$ obtained from photoionization of $C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1)$, $J' = 8$. The $C_2H_2^+$ ion intensities have been normalized by the corresponding VUV intensities. As expected, this spectrum reveals a series of well-resolved autoionizing peaks in the VUV region above 11.0 eV . Below 11 eV , the photoion intensity is at the noise level. The photoion spectrum for $C_2H_2^+$ obtained from $C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1)$, $J' = 10$ is depicted in Fig. 1(b). This spectrum has similar autoionizing

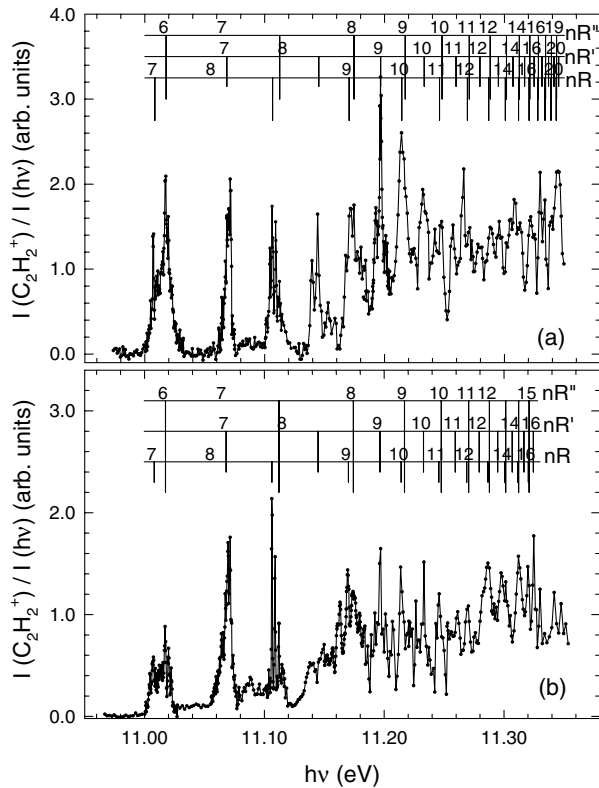


FIG. 1. IR-VUV photoion spectra for $C_2H_2^+$ in the VUV range of 10.97–11.35 eV obtained with the IR-OPO frequency set at (a) the $P(9)$ and (b) the $P(11)$ transitions of ν_3 . The labels on top mark the assignment of the three Rydberg series (nR , nR' , and nR'') converging to the excited $\nu_3^+ = 1$ state of the ion. The assigned positions correspond to VUV energies of the $\Delta J = 0$ transitions.

features as those resolved in Fig. 1(a), although the energy positions of the autoionization peaks are slightly different because of the difference in the initial J' values.

In order to ascertain that the photoions originate from excited $C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1)$, we measured the $C_2H_2^+$ photoion intensities by fixing the VUV energy at a number of autoionization peaks resolved in Figs. 1(a) and 1(b) and scanning the IR-OPO frequency. The IR spectra thus obtained show well-resolved rotational transitions for the ν_3 band, proving that the photoion spectra of Figs. 1(a) and 1(b) are truly rovibrationally selected photoionization spectra originating from the respective $J' = 8$ and 10 levels of $C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1)$. A sample IR spectrum is shown in Fig. 2, revealing the $P(9)$ and $P(10)$ transitions for the $C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1)$ band. The weak $P(3)$ and $P(4)$ transitions for the $\nu_2 + \nu_4 + \nu_5$ combination band are also discernible. The observed linewidths for the $P(9)$ and $P(10)$ transitions indicate that the optical bandwidth for the IR-OPO is $\approx 0.1 \text{ cm}^{-1}$.

Knowing the IE [10,15] of C_2H_2 and the IR energy for the $P(9)$ transition, we calculated the ionization threshold for the $J' = 8$ level of $C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1)$ to be 10.995 eV. However, the spectra of Figs. 1(a) and 1(b) show little evidence of a photoion continuum commencing

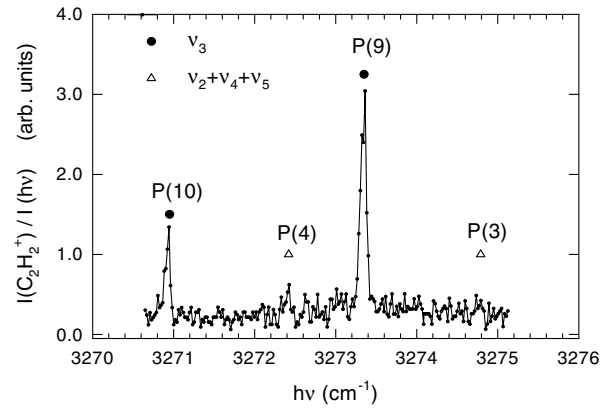


FIG. 2. The IR absorption spectrum for $C_2H_2(\tilde{X}^1\Sigma_g^+)$ in the IR region of 3270.6–3275.2 cm^{-1} , revealing the $P(3)$ and $P(4)$ transitions of the $\nu_2 + \nu_4 + \nu_5$ combination band and the $P(9)$ and $P(10)$ transitions of the ν_3 band. The VUV energy is fixed at the autoionizing Rydberg state $6R''$ at 11.0164 eV.

at that 10.995 eV. This observation is consistent with the FCF calculation [14] and selection rules, predicting a zero FCF for the formation of $C_2H_2^+$ in its ground state from photoionization of $C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1)$. Considering that the resolved resonance peaks appearing in the range of 11.00–11.35 eV are autoionizing Rydberg states converging to $C_2H_2^+(\tilde{X}^2\Pi_u; \nu_3^+ = 1)$, we have successfully assigned these resonances using the Rydberg equation: $E_{\text{obs}} = \text{IE}(J', N^+) - R/(n - \delta)^2$. Here, E_{obs} is the VUV energy in eV for the observed autoionizing peak, $\text{IE}(J', N^+)$ is the IE from the J' rotational level of $C_2H_2(\tilde{X}^1\Sigma_g^+; \nu_3 = 1)$ to the rotational ionic state N^+ of $C_2H_2^+(\tilde{X}^2\Pi_u; \nu_3^+ = 1)$, R (13.6054 eV) is the Rydberg constant, n is the principal quantum number, and δ is the quantum defect. The $\text{IE}(J', N^+)$ values can be calculated using the precisely measured IR frequencies and rotational constants [11,20] for the neutral and ion. The ground electronic configuration for C_2H_2 suggests the existence of four major Rydberg series nR , nR' , nR'' , and nR''' [21]. The nR' and nR''' are nearly degenerate. We have assigned the observed autoionizing features by fitting the peak positions to the three different Rydberg series nR , nR' , and nR'' using the Rydberg equation with δ as the fitting parameter and setting $J' = N^+ = 8$ or 10 ($\Delta J = 0$ transition). As marked in Figs. 1(a) and 1(b), nearly all of the resonance peaks are assigned. The measured energies and the fitted term values agree to within 1 standard deviation of the VUV resolution of 0.5 meV for 21 out of 24 lines and all are within 2 standard deviations. The present results show that the Rydberg states with the $\nu_3^+ = 1$ ion core decay efficiently into the ionization continuum of $C_2H_2^+(\tilde{X}^2\Pi_u)$ in its ground vibrational state and that the autoionization occurs as soon as it is energetically allowed. Vibrational autoionization is a likely mechanism for the observation of these Rydberg states.

The δ values for the Rydberg series nR (0.958 ± 0.005), nR' (0.405 ± 0.005), and nR'' (-0.122 ± 0.005) converging to $\nu_3^+ = 1$ obtained here are all slightly lower

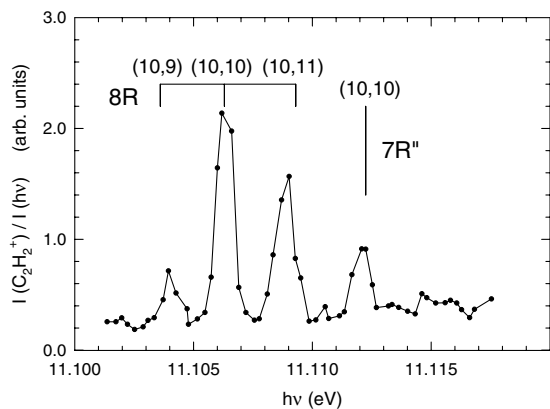


FIG. 3. Observed rotational structures of the $7R''$ and $8R$ Rydberg states of acetylene. The labels show the rotational (J', N^+) assignment of the level. N^+ is the convergent rotational quantum number of the $\nu_3^+ = 1$ state.

than the corresponding δ values observed in absorption [21] for nR (0.976), nR' (0.470), and nR'' (-0.094) converging to the ground state of the ion. The δ values for nR (0.95) and nR' (0.36) converging to $\nu_2^+ = 1$ obtained in a previous VUV-photoionization study [16] are less precise. Nevertheless, they are also lower than those converging to the ground state ion. These slight differences in δ values reflect the effect due to the distortion of the ion core along the ν_2^+ and ν_3^+ coordinates with respect to the equilibrium geometry of the ion core. By employing the IR-VUV photoionization approach, it should be possible to perform systematic studies of the vibrational effect on quantum defects for autoionizing Rydberg series of polyatomic molecules.

A careful examination of the spectra of Figs. 1(a) and 1(b) reveals that the autoionization resonances at 11.02 and 11.11 eV exhibit discernible fine structures. An expanded view (Fig. 3) of the peak at 11.11 eV of Fig. 1(b) reveals four peaks spaced ~ 2 meV apart. Assuming the $\Delta J = 0, \pm 1$ autoionization selection rules, we have assigned three of these peaks to rotational features of the $8R$ Rydberg state converging to the rotational levels $N^+ = 9, 10,$ and 11 of the $\nu_3^+ = 1$ ionic state. The extracted rotational constant of $B^+ = 1.10 \text{ cm}^{-1}$ is in excellent agreement with the literature value [11]. From the deconvoluted peak width (3 cm^{-1}) for these rotational transitions, the lifetime for these rotational levels of the $8R$ Rydberg state is estimated to be ~ 1.8 ps. The latter value is in the same range as the lifetimes for the ungerade Rydberg states converging to the $\nu_2^+ = 1$ state [22]. The remaining peak of Fig. 3 is attributed to the $\Delta J = 0$ transition of the $7R''$ Rydberg state. The $\Delta J = \pm 1$ peaks of the $7R''$ state are too weak to be observed. The similar structures resolved in Fig. 1(a) have been assigned with the same degree of rotational precision.

To our knowledge, this is the first time that photoionization processes of state-selected molecules are examined employing a high-resolution VUV-synchrotron

source. The unique combination of a broadly tunable VUV-synchrotron radiation and the high-repetition-rate IR-OPO shall open the opportunity to many future studies in state-selective photoionization and photoelectron phenomena. Future VUV pulsed field ionization-photoelectron measurements of rovibrational-state-selected neutrals prepared by IR excitation will provide valuable information on state-to-state photoionization dynamics.

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