Vibrational autoionization of state-selective jet-cooled methanethiol (CH$_3$SH) investigated with infrared + vacuum ultraviolet photoionization

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[Abstract] Vibrational photoionization efficiency (PIE) spectra of jet-cooled methanethiol (CH$_3$SH) were recorded by excitation of CH$_3$SH to a specific vibrationally excited state with an infrared laser, followed by a tunable laser light in the vacuum ultraviolet region for ionization. Autoionizing Rydberg states, assigned to the *ns*, *np*, *nd* and *nf* series, were identified. When the IR excitation at 2601 (ν_3, SH stretch) and 2948 cm^{-1} (ν_2, CH$_3$ symmetric stretch) was employed, the Rydberg series converged to the respective vibrationally excited states (ν_3 and ν_2) of CH$_3$SH$^+$. When the IR excitation at 3014 cm^{-1} (ν_1/ν_9, mixed CH$_3$ antisymmetric stretches) was employed, two converging limits towards vibrationally excited states (ν_1 and ν_9) of CH$_3$SH$^+$ were observed. In addition, when the IR excitation at 2867 cm^{-1} ($2\nu_{10}$, overtone of CH$_3$ deformation) and 2892 cm^{-1} ($2\nu_4$, overtone of CH$_2$ scissor) was employed, both $\Delta v = -1$ and -2 ionization transitions were observed. In all spectra, the *ns* and *nd* series show more intensity than the other Rydberg series, which is consistent with the fact that HOMO is a *p*-like lone pair orbital on the S atom.

[Introduction] Vibrationally excited autoionizing Rydberg states, having a vibrationally excited ion core and a Rydberg electron, are superexcited states that lie above the first ionization threshold. Vibrational autoionization, a form of radiationless transition, can occur readily in these states through the conversion of vibrational energy into electronic energy of the electron to be ejected, resulting in a free electron and an ion.[1, 2]

In general, these superexcited states are difficult to prepare with single-photon excitation because of the poor Frank-Condon overlap. They may be prepared via two-photon or multi-photon excitation. The most common method employs the Rydberg-Rydberg transition, in which the molecule is first excited to a Rydberg state below the ionization threshold with one or two photons in the ultraviolet (UV)/visible range; this Rydberg state is subsequently excited to a high-lying autoionizing state with another photon. The second method employs Rydberg excitation of a vibronically excited state, in which the molecule is first excited with an UV laser to a specific excited vibrational level of the electronically excited state, which is subsequently excited with a second UV photon to the high-lying autoionizing states.

In this work, we performed IR-VUV two-color photoionization experiments on jet-cooled CH$_3$SH by firstly exciting CH$_3$SH to a specific vibrationally excited state with an IR laser, followed by excitation to the auto-ionizing Rydberg states with a tunable VUV laser. Distinct from that of the single-photon VUV photoionization efficiency (PIE) spectrum of CH$_3$SH, many features appeared and were assigned to four autoionizing Rydberg series converging to the vibrationally excited states of CH$_3$SH$^+$.

[Methods] The experimental apparatus consisted of a supersonic jet, two laser systems, and a time-of-flight mass spectrometer. Jet-cooled gaseous CH$_3$SH (2%) seeded in Ne was produced on supersonic expansion of the mixture through a pulsed Even–Lavie valve (10 Hz) with a stagnation pressure ~2 atm. The IR-VUV-PIE spectra were recorded by exciting the molecule to a specific vibrationally excited state with IR light at a fixed wavenumber and scanning the

wavenumber of the VUV laser light while monitoring the CH_3SH ion signal.

[**Results and Discussion**] The IR-VUV-PIE spectrum of CH_3SH in Fig. 1 was recorded with excitation of the SH-stretching (v_3) mode of CH_3SH at 2601 cm^{-1}. Values of ionization energy (IE, 76256 cm^{-1})[3] and IE + v_3^+ (78758 cm^{-1}) are indicated with black dotted lines in Fig. 1. Some weak bands with distinct structures appeared when the total excitation energy is above the IE near 76256 cm^{-1}, indicating that some ionization took place through vibrational autoionization. The ion signal increased abruptly at wavenumbers corresponding to IE + v_3 near 78860 cm^{-1} because the direct ionization of CH_3SH in its ground state became dominant when the VUV light exceeded the IE. The

Fig. 1. The IR-VUV-PIE spectrum of CH_3SH obtained with IR excitation of v_3 at 2601 cm^{-1}.

wavenumbers of these lines were fitted to the Rydberg expression. Four Rydberg series with quantum defects $\delta = 0.33 \pm 0.01$, 2.11 ± 0.01, 1.53 ± 0.01 and -0.03 ± 0.01, were identified, all with a converging energy of $IE_v = 78770 \pm 10$ cm^{-1}, which is similar to IE (= 76256 cm^{-1}) plus the vibrational excitation energy 2502 cm^{-1} (v_3^+) of CH_3SH^+.

The IR-VUV-PIE spectrum of CH_3SH in Fig. 2 was recorded with excitation of the CH_3-deformation overtone $(2v_{10})$ mode of CH_3SH at 2867 cm^{-1}. Three Rydberg series with quantum defects $\delta = 0.33 \pm 0.01$, 2.12 ± 0.01, and 1.56 ± 0.01 were identified. The IE and IE + v_{10}^+ (~77630 cm^{-1}) are marked as black dotted lines in Fig. 2. Although with less intensity, the Rydberg series appeared also below total energy of 77630 cm^{-1} (IE + v_{10}^+), indicating that the vibrationally autoionization propensity rule of $\Delta v = -1$ does not hold strictly. The background of the PIE curves in Figs. 1 and 2 are nearly zero for total energy less than ~78600 cm^{-1}, indicating that even when the total energy of the IR +

Fig. 2. The IR-VUV-PIE spectrum of CH_3SH obtained with IR excitation of $2v_{10}$ at 2867 cm^{-1}.

VUV photons exceeds the IE, direct ionization is negligible.

By exciting the CH_3SH to other vibrational states while scanning the VUV light, the corresponding vibrational-state-selected autoionization PIE spectra were obtained. The converging limits, the quantum defects, and the average quantum yields of the vibrational-state-selected autoionizing series will be discussed.

[**References**]

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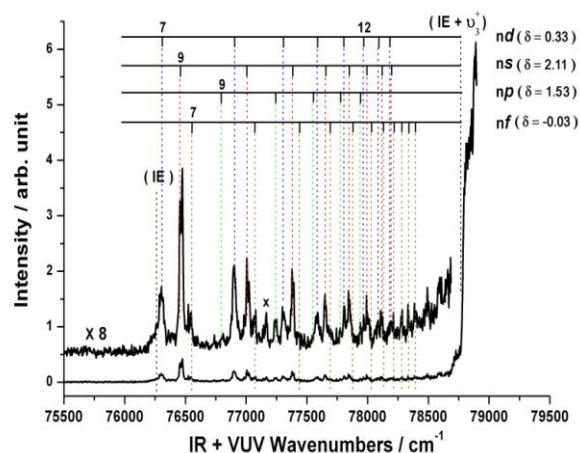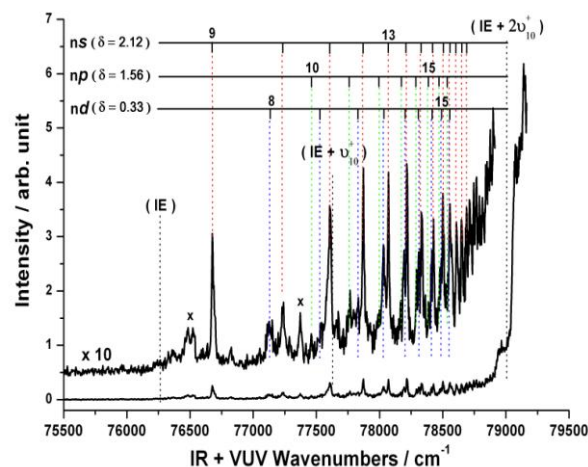[3] Y. S. Cheung, J. C. Huang and C. Y. Ng, *J. Chem. Phys.*, 1998, **109**, 1781.