Multiply excited molecules in electron collisions as probed by energy and angle-resolved coincidence measurements between a scattered electron and a photon from a fragment atom

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Abstract. Doubly excited states of CH₄ in electron collisions were investigated for the first time by measuring electron energy-loss spectra tagged with the emission of the Lyman-α photon. It turned out that the collisional cross section resulting in the emission of the Lyman-α photon originating from the doubly excited states are larger than or comparable to those originating from the nearby singly excited states and the electron interaction with molecules promotes the double excitation against the single excitation as compared with the photon interaction.

1. Introduction

Multiply excited states of molecules are highly correlated systems involving light and heavy particles strongly interacting with each other and thus revealing the dynamics of them in electron collisions is one of important and challenging subjects in physics and chemistry. However, it has been difficult to observe the multiply excited molecules until we established a new experimental method based on the coincidence detection between a scattered electron and a photon emitted from an excited neutral fragment, i.e. the coincident electron-energy-loss spectroscopy [1]. The key to observing the multiply excited states embedded in ionization continua is measuring the cross sections free from ionization. In the present paper, the recent investigations on the the dynamics of multiply excited states of CH₄ in electron collisions [2–4] are presented. The density of the dipole oscillator strength for the emission of the Lyman-α fluorescence in the photoexcitation of CH₄ was measured as well since the comparative study between electron and photon interactions gives us a deeper understanding of the multiple excitation [2, 5].

These studies strongly motivated by our previous measurements of the cross sections for the emission of dispersed fluorescence from neutral atoms and radicals produced in the photoexcitation of CH₄ NH₃ and H₂O [6–8]. We found that the dipole oscillator strengths for the emission of the Balmer fluorescence originating from the doubly excited
states are larger than or comparable to those from the nearby singly excited states, which seems to indicate the breakdown of the independent electron model.

2. Experiment

The experimental apparatus is composed of an electron energy loss spectroscopy system for static gas target, a Lyman-α photon detector and a delayed coincidence system. Electrons scattered into a small solid angle were energy-analyzed by a hemispherical electron energy analyzer and detected by a channel electron multiplier. True coincidence rates were normalized for the target gas density, incident electron beam current and geometric factor to obtain differential cross sections for electron scattering accompanied by the emission of the Lyman-α photon, \( d^3\sigma/dE d\Omega_e d\Omega_{ph} \), where \( d\Omega_e \) and \( d\Omega_{ph} \) are elements of solid angles for the scattered electron and emitted photon, as a function of energy loss \( E \), i.e., the coincident electron-energy-loss spectrum. Details of the experiments were described in [2] and [5].

For the measurement of the scattering angle dependence of the coincident electron energy loss spectra, we developed a new apparatus using an imaging detector, i.e., we employed an electron energy analyzer equipped with a position sensitive detector [3]. The fast-slow coincidence technique between energy-dispersed electrons and Lyman-α photons enable simultaneous accumulation of the coincidence time spectra at different energy losses and hence the time needed for measuring one coincident electron-energy-loss spectrum was greatly reduced as compared with that by the apparatus mentioned above. To put the coincident energy loss spectra measured at different scattering angles on the same vertical scale, we calculated the geometrical factor as a function of electron energy loss and scattering angle based upon the simulation of the trajectories of scattered electrons and emitted photons.

Measurement of the density of the dipole oscillator strength for the emission of the Lyman-α photon in the photoexcitation of CH\(_4\) as a function of incident photon energy were carried out at the BL-20A of the Photon Factory, KEK. Linearly polarised light from a 3m normal incidence monochromator was introduced into a gas cell equipped with the Lyman-α photon detector which is the same as that used in the electron collision experiment. The details were mentioned in [2] and [5]. In this paper we use the same symbol \( E \) for the energy loss and incident photon energy because both quantities give the excitation energy of the target molecule.

3. Result and discussion

The coincident electron-energy-loss spectrum of CH\(_4\) measured at incident electron energy of 80 eV and electron scattering angle of 10° (hereafter abbreviated as ”80eV/10°”) is shown in fig. 1(b) together with the ordinary electron-energy-loss spectrum of CH\(_4\) measured at 80eV/10° in (a). It is noted that superexcited states of CH\(_4\) are clearly visible in fig. 1(b) owing to the coincidence detection of the scattered...
The electron energy-loss spectra of CH$_4$ measured at 80 eV incident electron energy and 10° electron scattering angle [2]: (a) the ordinary energy-loss spectrum, (b) the spectrum tagged with the emission of the Lyman-α photons, i.e. the coincident energy-loss spectrum. The curves in (b) show the results of the fits (see text). The square of the momentum transfer, $K^2$, is indicated on the upper axis.

Figure 1.

The superrexcited states of CH$_4$ take also part in the emission of the Lyman-α photon following the photoexcitation. In fig. 2(b) the density of the dipole oscillator strength (DOS) for the emission of the Lyman-α photon, $(dJ/dE)_{Ly-α}$, is shown as a function of incident photon energy $E$. The DOS curve was decomposed into five contributions from superrexcited states at 20.3, 22.1, 29.5, 34.7 and 38.6 eV by a fit based on the multi-dimensional reflection approximation [9] and a semiclassical treatment of the decay dynamics of the superrexcited states involved. The peaks at 20.3 and 22.1 eV were well investigated by various experimental methods and assigned to the singly excited $(2a_1)^{-1}(3pt_2)$ and $(2a_1)^{-1}(4pt_2)$ superrexcited states [6]. It followed from the vertical ionization potentials for the $(1t_2)^{-1}$ (14.5 eV), $(2a_1)^{-1}$ (23.0 eV) and $(1a_1)^{-1}$ (290.707 eV) states of CH$_4^+$ that the other three peaks are attributed to nothing other than the doubly excited states. Kato et al [6] found three doubly excited states of CH$_4$, D1, D2 and D3, in the densities of the dipole oscillator strength for the emission of Balmer series and CH(A, B→X) fluorescence as a function of incident photon energy in the photoexcitation of CH$_4$. On account of the energy positions and peak widths the peaks at 29.5 and 34.7 eV in fig. 2(b) seem to be attributed to the doubly excited D2 and D3 states, respectively. The 38.6 eV peak seems to originate from the newly found doubly excited state, which was labelled D4. It was found that the DOS originating from the doubly excited D2 - D4 states are larger than or comparable to those from the nearby singly excited $(2a_1)^{-1}(npt_2)$ ($n=3,4$) states, which seems to indicate the breakdown of the independent electron model.

In fig. 2(b) the energy positions of the four correlation states of CH$_4^+$ found in the X-ray photoelectron spectrum of CH$_4$ [10] are shown by vertical bars. It turned out from the viewpoint of energy that the doubly excited D2 - D4 states are built on the correlation states of CH$_4^+$ since a doubly excited state, i.e. two-particle/two-hole state, is expected to lie in a lower energy-range than the energy of the corresponding correlation state, i.e. one-particle/two-hole state, as an ion-core. In conclusion, the
doubly excited D2, D3 and D4 states are built on the \((1t_2)^{-2}(3a_1), (2a_1)^{-1}(1t_2)^{-1}(2t_2)\) and \((2a_1)^{-2}(3a_1)\) states of CH_4^+[10].

The coincident electron energy-loss spectrum was decomposed into the five contributions from the superexcited states by the similar fitting procedure as is shown in fig. 1(b). The superexcited states are the same as those in fig. 2(b). It is interesting that the cross sections originating from the doubly excited states are larger than or comparable to those originating from the nearby singly excited \((2a_1)^{-1}(npt_2)\) \((n=3,4)\) states. We note that forbidden superexcited states make almost no contribution in the coincident electron energy-loss spectrum at 80 eV/10°, while optically forbidden doubly excited states make a clear contribution at 100 eV/8° electron collision with NH_3 [5].

Formation of the doubly excited D2 - D4 states of CH_4 by photon and electron interactions is discussed in terms of the oscillator strengths as follows. The cross section excited states make a clear contribution at 100 eV/8° electron collision with NH_3 [5].

Figure 2. (a) The density of the effective generalized oscillator strength for the emission of the Lyman-α photon in CH_4 at 80 eV incident electron energy and 10° electron scattering angle, \((dF/dE)_\alpha\), as a function of electron energy-loss \(E\) and (b) the density of the dipole oscillator strength for the emission of the Lyman-α photon in CH_4, \((dF/dE)_\alpha\), as a function of incident photon energy \(E\). The curves show the results of the fits (see text). The vertical bars in (b) represent the energies of the correlation states of CH_4^+[10].

\[
\frac{d^3\sigma_\alpha}{dE d\Omega_e d\Omega_{ph}} = \frac{k_s}{k_i} \frac{4R_g}{E} \frac{1}{K^2} \frac{1}{4\pi} \left( \frac{dF_\alpha(K, k_i)}{dE} \right)_{\alpha, Ly} ,
\]

where \(k_i\) and \(k_s\) are the magnitudes of the wavenumber vectors of the incident and scattered electrons, respectively, \(R_g\) the Rydberg energy and \(K\) the momentum transfer [11]. According to the limit theorem [12, 13],

\[
\left( \frac{dF_\alpha(K, k_i)}{dE} \right)_{\alpha, Ly} \rightarrow \left( \frac{df_\alpha}{dE} \right)_{\alpha, Ly}
\]
as the momentum transfer \(K \rightarrow 0\). Fig. 2(a) shows \((dF(K, k_i)/dE)_{Ly, \alpha} = \sum_\alpha dF_\alpha(K, k_i)/dE)_{Ly, \alpha}\) as a function of energy loss \(E\). It was concluded from figures 2(a) and (b) that the electron interaction with CH_4 at 80eV/10° involves the mechanism that enhances the double excitation against the single excitation as compared with the photon interaction. The photon interaction is expressed by a sum of single-electron
dipole operators. The same conclusion was also obtained in the study on the electron (100eV/8°) and photon interactions with NH₃ [5].

To investigate further the electron-CH₄ collision to form the doubly excited states, the coincident electron energy loss spectra were measured at 80 eV incident electron energy and electron scattering angles of 4°, 12°, 24°, 36° and 48° [4]. The spectral shape changes drastically with increasing the electron scattering angle. All the coincident energy-loss spectra were decomposed into the contributions from the same singly and doubly excited states as those in fig. 2(a) and no discernible contribution of optically forbidden doubly excited states was observed up to 48°. It is remarkable that the fraction of the doubly excited D4 state increases and that of the doubly excited D2 state decreased with increasing the electron scattering angle. The details will be given in [4].

4. Conclusions

We measured electron energy-loss spectra of CH₄ tagged with the emission of the Lyman-α photon, i.e. the coincident electron-energy-loss spectra, and the density of the dipole oscillator strength for the emission of the Lyman-α photon to investigate the double excitation in electron and photon interactions. The doubly excited states of CH₄ contributing to the emission of the Lyman-α photon were revealed for the first time. The density of the dipole oscillator strength seems to show the breakdown of the independent electron model: the dipole oscillator strengths originating from the doubly excite states are larger than or comparable to those originating from the nearby singly excited states. It turned out that the cross sections of the electron interaction originating from the doubly excited states are also larger than or comparable to those originating from the nearby singly excited states and the electron interaction promotes the double excitation against the single excitation as compared with the photon interaction.

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