Possibility of experimental determination of the frequencies of autoionization decay of excited molecular states

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Using as an example the study of collisions between closely approaching atoms of metastable He*(2^3S) and Ar(^1S), we demonstrate the possibility of determining the interaction potential and the width of the autoionization level of a system, from experimental data on the differential scattering.

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The decay frequency (or the level width) is a most important characteristic of a quasistationary state and its nonempirical calculations are extremely difficult. Collisions with Penning ionization (PI) form a convenient object for a detailed study of one of the types of decay, namely autoionization decay. Practically all the recent PI investigations[1] have been confined to thermal velocities, and information on the interaction potentials and on the level widths has been obtained for distances that exceed the characteristic molecular dimensions.

In this paper we attempt to overcome this limitation by studying the differential scattering (DS) of fast beams of metastable He*(2^3S) atoms in argon, in a range of angles corresponding to small approach distances. The idea of the experiment is based on measurement of the DS at different relative velocities (beam energy $E = 400$, 600, 1200, and 2000 eV); this makes it possible, by virtue of the invariance of the terms of the excited and ionic states of the quasimolecule, to connect the changes in the observed scattering picture with the variation of the transition probabilities.

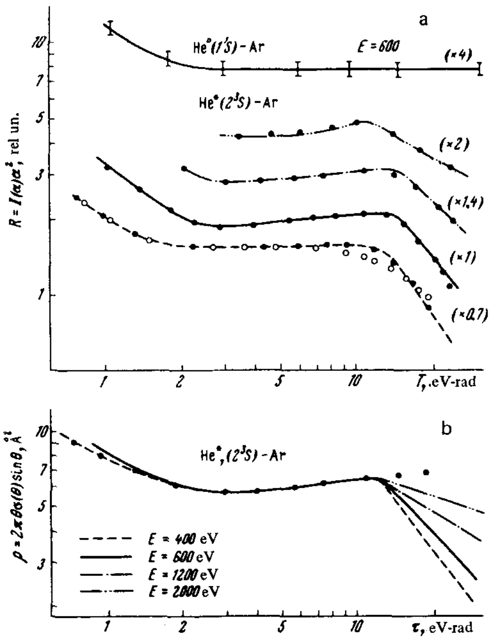
We used a setup similar to that described in[2]. The He* beam was obtained by charge exchange of He$^+$ ions in Na vapor. The beams were registered with a channel multiplier; at the investigated beam energies, the discrete-counting efficiency was the same both for He atoms in the ground state and in the metastable state. The experimentally measured quantity is the total current $I(\alpha)$ of the elastically and inelastically scattered particles gathered by the detector in a given angular position, and connected with the differential scattering cross section $[\sigma_t(\theta) = \sigma_{el}(\theta) + \sigma_{inel}(\theta)]$ in the laboratory frame by a simple relation of the convolution type

$$I(\alpha) = A\int \sigma_t(\theta) f_\alpha(\theta) \sin\theta \, d\theta \qquad (1)$$

A is a constant known from the experimental conditions, and $f_\alpha(\theta)$ is the apparatus function.[2] Expression (1) can be used for the inversion procedure, i.e., for finding the cross section $\sigma_t(\theta)$ that describes the measured current $I(\alpha)$.

The lines plotted in Fig. a in the relative coordinates $R = I(\alpha)\alpha^2$ and $T = \alpha E$, represent the results of the measurements for different He* beam energies (the figure shows also a plot of $I(\alpha)$ for the scattering of the atoms in the ground state; the vertical strokes give the typical spread of the individual measurements). In Fig. b, the lines in the relative coordinates $\rho = 2\pi\sigma(\theta)\,\theta\,\sin\theta$ and $\tau = \theta E$ represent the cross sections $\sigma_t(\theta)$ reconstructed from the measured currents. As seen from the figures, the scattering picture typical of metastable-atom collisions differs from that for He(I, S), with a sharp decrease of the $R(T)$ and $\rho(\tau)$ curves in the region of the relative angles T, $\tau > 12$ eV-rad. We also see distinctly that the rate of decrease depends on the energy. These features serve as a potential source of information on the decay frequency ν, which is described by the level width $\Gamma(r)(\nu = \Gamma(r)/\hbar)$. The qualitative and quantitative interpretation of these features, which are due to Penning ionization, can be readily obtained by treating the collisions of the He* and Ar atoms as scattering with vertical transitions between the terms of the excited state $V^*(r)$ and the final ionic state $V^+(r)$ of the quasimolecule. On moving along the trajectory, this vertical transition "switches over" the interaction via the potential V^* into an interaction via V^+.

It is seen from Fig. b that up to $\tau \sim 12$ eV-rad the relative cross sections $\rho(\tau)$ for different energies fit a single curve. This means that the section $\tau < 12$ eV-rad corresponds to pure elastic scattering unperturbed by transitions, $\sigma_t(\theta) = \sigma_{inel}(\theta)$, and can be used to determine V^* from $\sigma_{el}(\theta)$. The best fit of the values of $\sigma_{el}(\theta)$ calculated with trial V^* (the points of Fig. b) is obtained



for a potential described by the polynomial $V^* = \sum_{m=0}^{5} a_n r^n$ (where r is in angstroms and V^* is in electron volts). The coefficients in the interval $r = 1.2$ to 2.65 Å are $a_0 = -6.398$, $a_1 = 114.50$, $a_2 = 2633.95$, $a_3 = 1449.02$, $a_4 = -1361.18$, and $a_5 = 464.15$, while for $r > 2.65$ Å we have $a_0 = a_1 = a_2 = a_3 = a_4 = 0$ and $a_5 = 44.84$. This potential yields in the region $r \sim 3.4$ Å values that agree with those obtained in experiments with thermal beams.[1]

The convolution (1) can be written in the classical approximation $[\sigma(\theta) = (b/\sin\theta) \mid db/d\theta \mid]$ in the following form, which is convenient for calculations:

$$I(\alpha) = A\{\iint b f_\alpha(\theta_{\text{in}}) P_{\text{in}}\, db\, dr + \iint b f_\alpha(\theta_{\text{out}}) P_{\text{out}}\, db\, dr + \int b P_{\text{el}} f_\alpha(\theta_{\text{el}})\, db\}. \tag{2}$$

Here $P_{\text{in}}(r, b)$ and $P_{\text{out}}(r, b)$ are the transition probability densities at the point r on the entrance and exit sections of the trajectory, $P_{\text{el}}(b)$ is the probability of survival of the excited state and accordingly of the elastic scattering; $\theta_{\text{in}}(r, b)$ and $\theta_{\text{out}}(r, b)$ are deviation functions determined by the interaction via composite potentials with a transfer $V^* \rightarrow V^*$ at the point r; $\theta_{\text{el}}(b)$ is the elastic-scattering angle for V^*. The deviation functions were calculated by the procedure proposed in[3]. The probabilities $P_{\text{in}}(r, b)$, $P_{\text{out}}(r, b)$, and $P_{\text{el}}(b)$ are connected in a known manner with $\Gamma(r)$.[4] If we neglect the $^2\Sigma - {}^2\Pi$ splitting of the HeAr$^+$ system, we can use for the effective V^+ an exponential approximation $[V^+ = 790 \exp(-3.9r)]$ of the values calculated in[5]. For an analytic description of the level width we have assumed the usual relation $\Gamma(r) = B \exp(-\beta r)$. Having in our possession information on the potentials V^* and V^+, we can obtain from the measured currents $I(\alpha)$ information concerning the parameters B and β.

The numerical fitting of $I(\alpha)$ was performed, using expression (2), with a BÉSM-6 computer by the Monte Carlo technique; a statistical accuracy of ~3% called for ~10^4 trajectories. The points in Fig. a show the calculated values of $R(T)$ for the parameters $B = 1240$ eV and $\beta = 5$ Å^{-1}. The parameters of[6] ($B = 27.2$, $\beta = 2.84$) result in worse agreement (circles in Fig. a).

The possibility of quantitatively describing the performed measurements, and the agreement between the calculated (for $B = 1240$ and $\beta = 5$) ionization cross sections $Q(E) = 2\pi \int b[1 - P_{\text{el}}(b)]\, db$ with independent measurements for $E = 400-1600$ eV,[7] allow us to conclude that the collision spectroscopy variant employed by us is indeed a convenient tool for determining the main characteristics of autoionization states. Analogous measurements were made for the systems He*-Kr, He*-Xe, and He*-H_2.

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