Photoionization Raman spectroscopy

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Experiments are reported on the photoionization detection of stimulated Raman scattering by electronic transitions of sodium in an atomic beam. There is a dip in the signal corresponding to the nonresonant two-photon ionization of sodium by electromagnetic radiation at $\lambda_1 = 284.5$ nm and $\lambda_2 = 1.06\,\mu$m. The dip is due to a Raman resonance at the forbidden $3s$–$4s$ transition.

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Raman spectroscopy has been a powerful tool for studying the structure of materials for many years now.[1] The advent of lasers made it possible to develop new methods of Raman spectroscopy, e.g., Dopplerless spectroscopy of the resonant stimuled Raman effect,[2] coherent anti-Stokes Raman spectroscopy (CARS),[3] and sub-Doppler saturation Raman spectroscopy.[4] Lasers have also made it possible to study vibrational-rotational spectra of gas-phase molecules which are inactive in absorption at particle densities up to $\sim 10^{12}$ cm^{-3} (Ref. 5). Optical methods have been used to detect the Raman effect.

In this letter we discuss the possibility of a photoionization method for recording stimulated Raman spectra, and we report experimental results on the detection of stimulated electron Raman scattering by transitions of sodium in an atomic beam. Figure 1 shows the energy level scheme of the Na atom, which we will use to illustrate the idea behind this method. The signal of interest may result from a competition between two-photon ionization (or, in general, many-photon ionization) and ordinary stimulated Raman scattering. In this transition scheme the total probability for the two-photon ionization of the atom by the time τ can be written as follows, according to the Breit-Wigner formula,[6] where the intermediate resonance at the $3s(n)$–$5p(m)$ transition is taken into account:
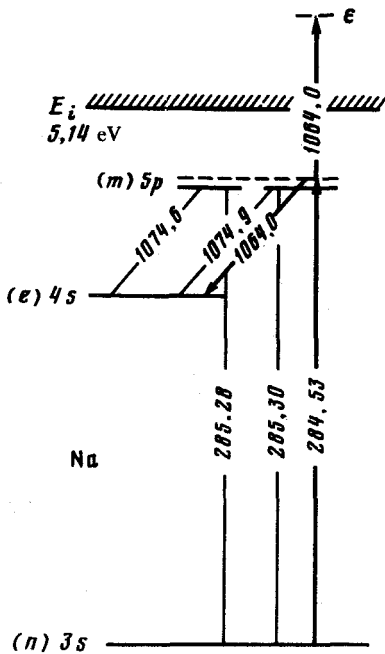
ε

E_i
5,14 eV   1064,0

(m) 5p   1074,6 1074,9 1064,0

(ε) 4s

285,28   285,30   284,53

Na

(n) 3s

FIG. 1. Working level scheme of Na. The wavelengths are given in nanometers.

$$W_i^{\,0} \approx 2\,\frac{\pi}{\hbar}\,\frac{|V_{nm}|^2\,|V_{m\epsilon}|^2}{\Omega^2+\gamma^2_m}\,\tau\,, \tag{1}$$

where $V_{nm} = a_{nm}E_1/2\hbar$ is the matrix element of the dipole interaction of the field with the atom at the $n-m$ transition, $V_{m\epsilon}$ is the matrix element of the transition from the resonant state m to the state of the ionization continuum with an energy $\epsilon = \hbar\omega_1 + \hbar\omega_2$, which is dipole-coupled with the resonant state, Ω is the difference between the frequency of the electromagnetic radiation and the frequency corresponding to the resonance with the atomic transition, and γ_m is the width of the resonant level, introduced phenomenologically. The quantity $|V_{m\epsilon}|^2 = (\hbar/2\pi)\Gamma_i$, where Γ_i is the ionization width of the resonant level,[6] can be calculated by the quantum-defect method from the Burgess-Seaton equations, given in Ref. 7, for example.

The probability for stimulated Raman scattering near resonance with electronic transitions in a biharmonic field can be written[2]

$$W_{SRS} \approx \frac{|V_{nm}|^2\,|V_{ml}|^2}{\Omega^2}\,\frac{\Gamma_{nl}\,\tau}{(\Omega_\mu-\Omega)^2+\Gamma_{nl}^2}\,, \tag{2}$$

where V_{nm} and V_{ml} are the matrix elements of the dipole interaction of the atom with the field at the transitions n-m and m-l, Ω and Ω_μ are the corresponding differences between the field frequencies and the resonant frequencies of the transitions, and Γ_{nl} is the width of the forbidden n-l transition.

It can be shown that when there are two channels by which an atom may leave the ground state the ionization probability can be written as

$$W_i \approx W_i^0 \ (1 - W_{\text{SRS}})$$ (3)

under the assumption $W_i^0 \ll W_{\text{SRS}}$, which is valid if $V_{m\epsilon} \ll V_{ml}$. It then follows from (1)–(3) that the total ionization probability is $(\Omega \gg \gamma_m, \tau\gamma_2 \gg 1)$

$$W_i \approx \frac{2\pi}{\hbar} \frac{|V_{nm}|^2 |V_{m\epsilon}|^2}{\Omega^2} \tau \left[1 - \frac{|V_{nm}|^2 |V_{ml}|^2}{\Omega^2} \frac{\Gamma_{nl} \ \tau}{(\Omega_\mu - \Omega)^2 + \Gamma_{nl}^2} \right] ,$$ (4)

It can be seen from (4) that the competition between channels should be manifested as a dip in the nonresonant photoionization signal as the frequencies of the electromagnetic radiation are tuned to the Raman resonance $\omega_1 - \omega_2 = \omega_{nl}$. By adjusting ω_1 or ω_2 one can record Raman-scattering spectra with a resolution limited by the Doppler effect, although even this effect could in principle be elminiated by one of several methods.

In the present experiments, a composite laser beam with two wavelengths, one fixed ($\lambda_2 = 1.064 \ \mu m$) and the other continuously adjustable in the ultraviolet part of the spectrum ($\lambda_1 = 284.0-290.0$ nm) is focused on a beam of sodium atoms produced by a thermal source in a vacuum chamber. The atomic beam interacts with the composite laser beam between parallel nickel plates, to which an accelerating voltage is applied. The Na$^+$ ions produced in the interaction volume are extracted through an aperture in one of the plates and sent to the cathode of a secondary electron multiplier. The pulsed output signal from the multiplier is amplified and measured with a coincidence circuit and a pulse counter. The tunable ultraviolet radiation is produced by using a lithium formate crystal for frequency doubling of the beam from a dye laser pumped by the second harmonic of a Nd:YAG laser in Q-switched operation with a high pulse repetition frequency (~ 4 kHz). The dye laser, which uses a free stream of rhodamine 6G in ethylene glycol, has a three-mirror resonator with astigmatism cancellation and a diffraction grating as dispersive element. An average power of about 1 mW was achieved at the wavelength $\lambda_1 = 284.5$ nm. The second wavelength was the output at the fundamental frequency of the Nd:YAG laser, with an average power ~ 1 W and a pulse length ~ 150 ns.

Figure 2 shows the results of measurements of the dependence of the sodium photoionization signal on the ultraviolet wavelength. At $\lambda_1 = 285.3$ nm there is an intense signal which corresponds to the saturated two-step ionization through the $5p$ state. As we leave the resonance, the signal drops sharply, and far from the resonance it corresponds to nonresonant two-photon ionization of Na from the ground state. The signal is slightly asymmetric, apparently reflecting a wavelength dependence of the photoionization cross section and also a possible contribution of the nonresonant excitation of real levels. At $\lambda_2 = 284.5$ nm we see a dip in the photoionization signal. The dashed line is the noise level in the system with $\lambda_2 = 1.06 \ \mu m$; this noise is generated by the ionization of Na atoms by photoelectrons ejected from the surfaces of the plates by scattered ultraviolet light. It can be seen from the Na level scheme that this dip results from a resonance at the Raman frequency corresponding to the forbidden $3s$–$4s$ transition. The width of the dip is determined in this case by the width of the output line from the Nd:YAG laser.
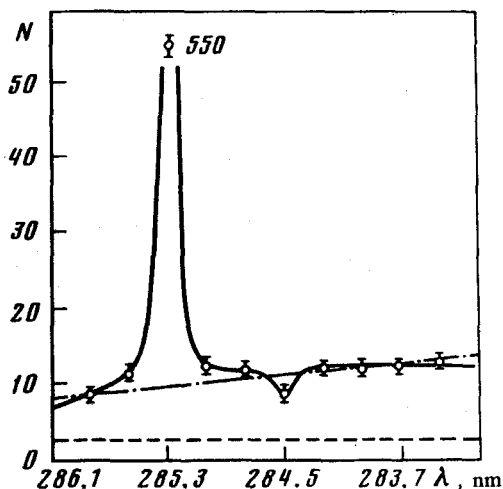
FIG. 2. Experimental dependence of the number of ion pulses per second (N) on the wavelength in the first step. The dashed line is the noise level.

In summary, these experiments directly demonstrate the possibility of photoionization detection of electron Raman scattering in sodium with a total of $\sim 10^5$–10^6 atoms in the interaction volume. We believe that the extension of this method to molecular systems will result in a sensitive and selective method for detecting molecules, including complex organic molecules, at exceedingly low concentrations. This method can furnish new information about the structure of these molecules and may prove an important supplement to the methods of photoionization mass spectrometry.[8]

[1]M. M. Sushchinskiĭ, Spektry kombinatsionnogo rasseyaniya zhidkosteĭ i kristallov (Raman Spectra of Liquids and Crystals), FM, Moscow, 1968; I. L. Fabelinskiĭ, Molekulyarnoe rasseyanie sveta (Molecular Light Scattering).
[2]I. M. Beterov, Yu. A. Matyugin, and V. P. Chebotaev, Zh. Eksp. Teor. Fiz. **64**, 1495 (1973) [Sov. Phys. JETP **37**, 756 (1973)].
[3]S. A. Akhmanov and N. I. Koroteev, Metody nelineĭnoĭ optiki v spektroskopii rasseyaniya sveta (Methods of Nonlinear Optics in Light-Scattering Spectroscopy), Nauka, Moscow, 1981.
[4]A.Owyoung and P. Esherick, Optics Lett. **5**, 421 (1981).
[5]R. L. Byer et al., in: Laser Spectroscopy V, Springer-Verlag, Heidelberg, 1981, p. 233.
[6]N. B. Delone and M. V. Fedorov, Trudy FIAN (Proceedings of the P. N. Lebedev Physics Institute, Vol. 115, 1980, p. 42.
[7]I. I. Sobel'man, Vvedenie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra), Nauka, Moscow, 1977.
[8]V. S. Antonov and V. S. Letokhov, Appl. Phys. **24**, 89 (1981); K. L. Kompa, Springer Series in Optical Sciences **26**, 7 182 (1981).

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