INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

J. Phys. B: At. Mol. Opt. Phys. **34** (2001) 2301–2312 www.iop.org/Journals/jb PII: S0953-4075(01)18908-X

Spectroscopy of quasimolecular optical transitions: Ca($4s^2\,{}^1S_0 \leftrightarrow 4s4p\,{}^1P, 4s3d\,{}^1D_2$)–He. The influence of radiation width

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Received 10 November 2000, in final form 18 April 2001

Abstract

We perform calculations using the semiclassical Fourier approach for quasimolecular spectra induced by thermal collisions of the excited calcium atom (Ca*) with the helium atom in the ground state (He) for the following quasimolecular optical transitions: ($\Omega = 0^+, 4s4p\,{}^1P$) $\leftrightarrow$ ($\Omega = 0^+, 4s^2\,{}^1S_0$) and ($\Omega = 0^+, 4s3d\,{}^1D$) $\leftrightarrow$ ($\Omega = 0^+, 4s^2\,{}^1S_0$) in the Ca–He quasimolecule. As a comparison with the experimental results obtained under gas-cell conditions, we average the spectra under study over the impact parameters and the Maxwellian distribution of the colliding particles. For the asymptotically forbidden Ca($4s^2\,{}^1S_0 \rightarrow 4s3d\,{}^1D_2$)–He quasimolecular transition, the first comparison between the calculated spectral line profile and the experimental one is made not only in shape, but also in absolute value. We clarify the physical mechanisms for the initiation of a spectral line satellite at the position of the forbidden atomic transition being investigated. The reasonable agreement confirms that the spectral lineshapes of the asymptotically forbidden transitions are formed due to the interplay between the structure of the potential energy curves involved and the strong dependence of the radiative width.

1. Introduction

The emission (and absorption) spectral lineshape for allowed transitions in atoms in a buffer-gas atmosphere is well understood both experimentally and theoretically. It contains a central Lorentzian part and quasistatic wings having some possible structure which can be assigned to the extrema in the difference potential curve. A similar general description for the spectral lineshape of the forbidden atomic transitions in a buffer-gas atmosphere is lacking.

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Such forbidden transitions are weak and difficult to measure experimentally. In this case corresponding spectral lines are formed by quasimolecular transitions only and have a wide variety of shapes, as the reasons for lifting a transition ban are varied. In contrast to the allowed transitions, the known analytical approaches, e.g. the quasistatic approximation or the unified Franck–Condon (UFC) theory [1], fail to describe the spectral lineshapes of asymptotically (at the limit of separated atoms) forbidden transitions [2]. The reason for this is that a strong dependence of quasimolecular radiative width on interatomic distance R is inherent in the forbidden transitions. As a result, there are few data on spectral lineshapes of asymptotically forbidden transitions and there are conflicting interpretations of the observed effects.

In that sense, the situation around the collisionally induced absorption line corresponding to the electric-quadrupole transition $4s^2\,{}^1S_0$–$4s3d\,{}^1D_2$ in calcium in a helium atmosphere is rather typical. The shape of such a transition spectral line is sensitive to the details of the quasimolecular potential energy curves (PEC) involved and to the radiation widths. The early experimental data obtained by the traditional photoabsorption hook method in absolute values for the spectral line of the forbidden transition in a rare-gas atmosphere were presented in [3]. The observed absorption spectrum shows a satellite with a maximum at $\omega = 22\,012$ cm^{-1}, shifted in the 'blue region' of the spectrum ($\Delta\omega = 162$ cm^{-1}) from the position of the corresponding atomic line $\omega_{\mathrm{at}} = 21\,850$ cm^{-1}. In [3] the satellite was associated only with the interaction of the $4s4p\,{}^1P_1$ and $4s3d\,{}^1D_2$ states at small interatomic distances. In more recent papers [4, 5] this transition for a variety of rare-gas perturber species was investigated by a laser probe fluorescence technique. Although the absorption spectral lineshape was not given in [4,5] directly for the case of helium, the data presented in [5, figure 3] provide an estimate of $\Delta\omega = 180$ cm^{-1}. The relative values obtained in experimental results were explained by the quasimolecular character of the absorption in the vicinity of a forbidden atomic transition. The results were interpreted in [5] in terms of molecular potentials and the satellite was concerned with the extremum in the corresponding difference potential curve.

Note that in the potential curve calculations, which existed at the time paper [5] was published, no data of the extremum occurrence were present. The first confirmatory evidence for the extremum in the difference potential curve was obtained in [6], where the satellite near the forbidden atomic transition was also assigned to this extremum. According to [6] the difference in energy values between the ${}^1D$ adiabatic term and the ${}^1S_0$ ground state (the difference potential curve ω_{SD}) does have an extremum at $R_{\mathrm{ext}} = 8.25$ au (see figure 1(*b*)). It is essential that the state interaction during the collision leads to a rapid change in the quasimolecular radiative width Γ relative to the interatomic distance R. Some preliminary estimates and calculations in [7] have shown that the strong dependence $\Gamma(R)$ can itself produce a maximum in the spectral profile.

In this paper we concentrate on clarifying the main mechanisms for the satellite formation in a spectral line of asymptotically forbidden transitions characterized by the absence of the corresponding atomic line. For the forbidden $\mathrm{Ca}(4s^2\,{}^1S_0 \rightarrow 4s3d\,{}^1D_2)$–He quasimolecular transition we obtained new experimental data and performed the original calculations within the framework of the semiclassical Fourier approach. The results were, for the first time, compared not only in shape, but in absolute magnitude.

We show in this paper that the UFC approach is unreliable for spectral lineshape calculations in the case of a strong dependence of the quasimolecular width on the interatomic distance, which is true for asymptotically forbidden transitions. We reveal that the spectral lineshapes of the asymptotically forbidden transitions are formed due to the interplay between the structure of the potential energy curves involved and the strong dependence of the radiative width. For spectrum calculations of such transitions an approach which takes into account both of these points simultaneously needs to be used. A good agreement between the experimental

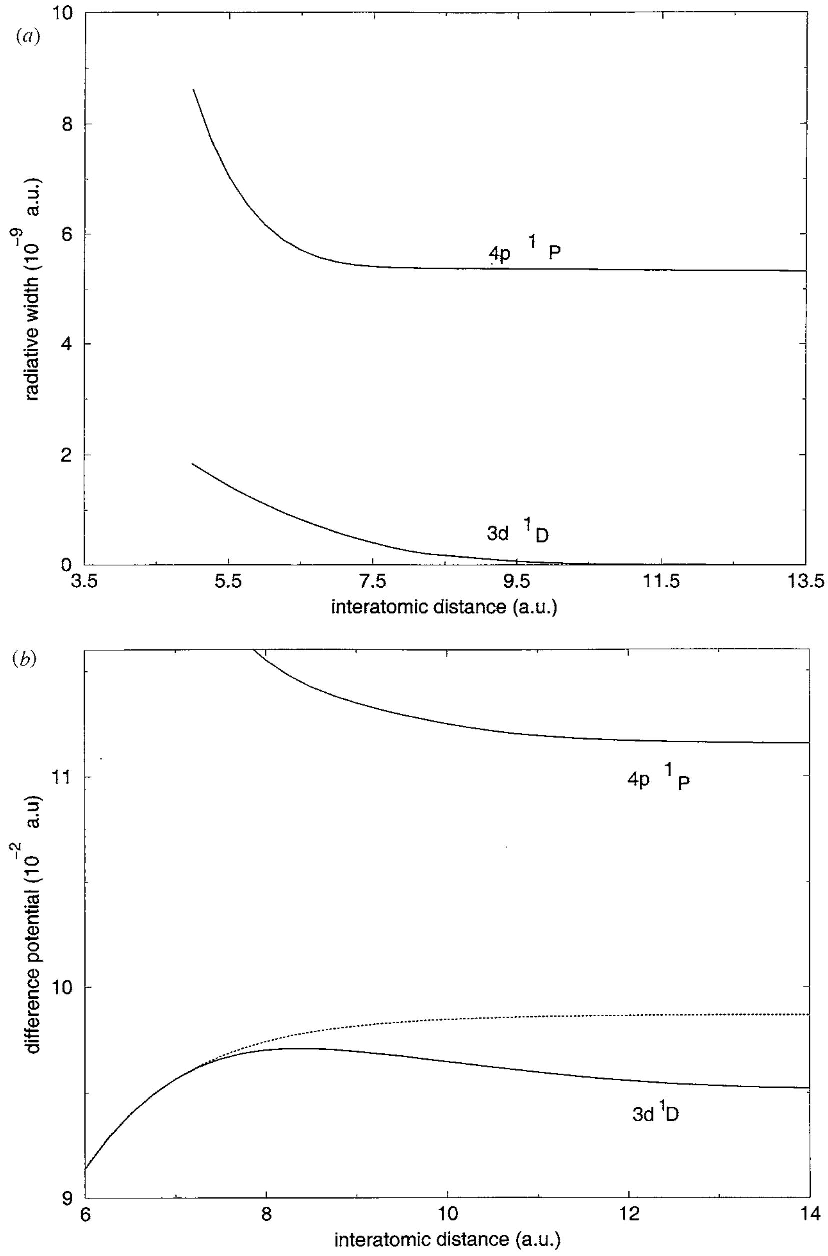

Figure 1. Radiative widths (*a*) and difference potential curves (*b*) for the ($\Omega = 0^+, 4s4p\,^1P$) and ($\Omega = 0^+, 4s3d\,^1D$) states of the Ca–He quasimolecule. The dotted curve in figure 1(*b*) is the exponential approximation for the ($\Omega = 0^+, 4s3d\,^1D$) difference potential curve.

and the calculated results shows that the semiclassical Fourier approach is the most adequate. Below it is shown that this approach fits well for the allowed transition Ca($4s^2\,^1S_0 \rightarrow 4s4p\,^1P$)–He also.

2. Experimental

The experimental set-up and procedures were almost the same as those described in our previous papers [8,9]. A heat-pipe metal-vapour cell (about 40 cm in effective vapour length) was placed in the test-beam section of a Mach–Zehnder interferometer and operated at temperatures of 1048 and 1163 K. The He perturber gas was added to the cell in the pressure range 100–700 Torr. The light beam from a Xe short-arc lamp is divided into two: one part passes through the absorption cell, while the other serves as a reference. These two light beams, and the interference beam which is the superposition of them, are alternately dispersed by a 50 cm Czerny–Turner spectrometer equipped with a grating of 600 or 1800 grooves/mm and are detected by a 1024-channel photodiode array. The overall resolution was about 0.1 nm. From the interference spectrum measured around the Ca resonance line, the number density of Ca atoms integrated over the line-of-sight, i.e. column density $N_{\mathrm{Ca}}l_a$, was determined very precisely.

Assuming that the absorption in the wings of the resonance line consists of a superposition of the absorption for the Ca–He pair and that of the Ca–Ca pair, we have

$$\frac{k(\Delta)l_a}{(N_{\mathrm{Ca}}l_a)^2} = \gamma_{\mathrm{CaHe}}(\Delta)\frac{n_{\mathrm{He}}}{N_{\mathrm{Ca}}l_a} + \frac{\gamma_{\mathrm{CaCa}}(\Delta)}{l_a} \tag{1}$$

where $\gamma_{\mathrm{CaHe}}(\Delta)$ and $\gamma_{\mathrm{CaCa}}(\Delta)$ are the reduced absorption coefficients at a wavenumber shift Δ from the line centre for the Ca–He and the Ca–Ca systems, respectively.

Thus, we can obtain γ_{CaHe} as a gradient and $\gamma_{\mathrm{CaCa}}/l_a$ as an intercept via the straight-line fit of the $kl_a/(N_{\mathrm{Ca}}l_a)2$ versus $n_{\mathrm{Ar}}/N_{\mathrm{Ca}}l_a$ plot at each Δ in the spectral range covered in this study. The experimental results obtained are shown in figures 2 (curve 2) and 4 (triangles). For the case of the asymptotically forbidden ($\Omega = 0^+$, 4s3d ^{1}D)–($\Omega = 0^+$, 4s^2 ^{1}S$_0$) quasimolecular transition, the spectral line profile has little in common with that for the allowed transition; the maximum shift from the atomic line position is $\Delta\omega = 200$ cm^{-1} centred at $\omega = 22\,050$ cm^{-1} with half-width 260 cm^{-1}.

3. Theory

3.1. Potential energy curves and radiative widths

In a rigorous approach one should first treat the quantum chemistry part of the problem, that is calculate the PEC and radiative widths (optical transition probabilities) of quasimolecular states associated with the atomic states involved. The (4s^2 ^{1}S$_0$–4s3d ^{1}D$_2$) transition is fully forbidden in the isolated Ca atom. In the process of interaction with the He buffer gas atom during the collision, three quasimolecular states with $\Omega = 0^+, 1, 2$ projection are produced from the atomic ^{1}D$_2$ state. The quasimolecular states with $\Omega = 0^+, 1$ are tied up with the ground $\Omega = 0^+$ state by optical transition. The required PEC of the excited states were obtained in [6] within the framework of the multi-configuration version of the pseudopotential method, but [6] contains no data for corresponding radiative widths. The simplest approach to the quasimolecular spectrum calculations may involve an approximation of the radiative width by its asymptotic value in the isolated atom. Indeed, this approach can be treated as a reasonable approximate estimate for the spectrum calculation of asymptotically allowed transitions, such as 4s^2 ^{1}S$_0$–4s4p ^{1}P. However, even such a simplistic approach is unsuitable for asymptotically forbidden transitions, since, in this case, there is a strong dependence of the radiative width on interatomic distance caused by the interaction between the excited diabatic states. The closeness of the excited diabatic states allows the application of a simple few-state or even a two-state, approximation as a reasonable model of the interaction [10].

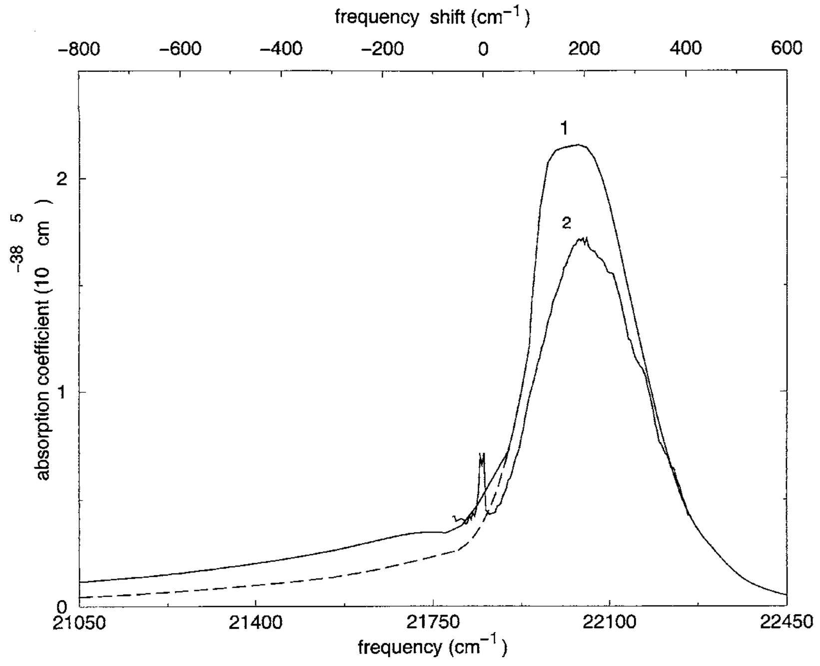

Figure 2. The absorption spectrum for the asymptotically forbidden ($\Omega = 0^+, 4s^2\,{}^1S_0$) $\rightarrow$ ($\Omega = 0^+, 4s3d\,{}^1D$) quasimolecular transition. Curve 1 shows the calculations in the semiclassical Fourier approach averaged over the impact parameters and the energies of colliding particles (the broken curve is the same, but with substitution of $R_0 \rightarrow R_c$); curve 2 is the experimental data for the spectrum.

The two-state approach was used in [7, 11] to calculate both the PEC and radiative widths of the quasimolecular states produced by the 4s4p ^{1}P and 4s3d ^{1}D atomic states of the Ca atom in collisions with the He atom. Results obtained in this way have demonstrated good agreement with those for PEC obtained within the framework of the multi-configuration version of the pseudopotential method.

Let us outline the method briefly for radiation widths starting with the $\Omega = 0^+$ states. We consider the interaction $V(R)$ between the two nearest interacting diabatic states connected with the ^{1}P and ^{1}D atomic states of $m = 0$ projection which is given by the following expression:

$$V(R) = \frac{V_0}{2} e^{-\alpha R}. \tag{2}$$

The parameters $V_0 = 0.96$ and $\alpha = 0.676$ were chosen from the calculated results on the non-diagonal part of the interatomic interaction. The corresponding adiabatic wavefunctions of investigated quasimolecular states are of the form:

$$\begin{aligned} \Psi(4\,{}^1P) &= \cos\theta(R)\varphi(4\,{}^1P) + \sin\theta(R)\varphi(3\,{}^1D) \\ \Psi(3\,{}^1D) &= -\sin\theta(R)\varphi(4\,{}^1P) + \cos\theta(R)\varphi(3\,{}^1D) \\ \theta(R) &= \tfrac{1}{2}\arctan\left(\frac{V_0}{\Delta\epsilon} e^{-\alpha R}\right) \end{aligned} \tag{3}$$

where $\varphi(3\,^1\mathrm{D})$ and $\varphi(4\,^1\mathrm{P})$ are wavefunctions of the atomic states involved, and $\Delta\epsilon$ is a splitting between the ^{1}P and ^{1}D excited states. Thus, according to equations (3) the radiative widths for the quasimolecular transition would be expressed as

$$\begin{aligned} \Gamma(0^+\,^1\mathrm{P}) &= \Gamma(^1\mathrm{P})\cos^2\theta(R)\left(\frac{\omega_{\mathrm{SP}}}{\omega_0}\right)^3 \\ \Gamma(0^+\,^1\mathrm{D}) &= \Gamma(^1\mathrm{P})\sin^2\theta(R)\left(\frac{\omega_{\mathrm{SD}}}{\omega_0}\right)^3 \end{aligned} \tag{4}$$

taking into consideration their dependence on the transition frequency (figure 1(*a*)). $\Gamma(^1\mathrm{P}) = 5.3\times10^{-9}$ au is the radiative width of the ^{1}P atomic state, ω_0 is the difference in energy values between the ^{1}P excited state and the ground state, ω_{SP} (ω_{SD}) is the difference in energy values between the ^{1}P (^{1}D) adiabatic term and the $^1\mathrm{S}_0$ ground state. Figure 1(*b*) shows the difference potential curves $\omega_{\mathrm{SP}}, \omega_{\mathrm{SD}} = \Delta U = U^* - U_0$ obtained by using the excited state potential curves U^* found in the two-level approach and the ground state potential U_0 taken from [12]. For a second pair of interacting states of $m = 1$ projection, the PEC and radiative widths were also calculated by the method given above, but in this case the parameters in (2) are $V_0 = 0.16$ and $\alpha = 0.832$.

3.2. Spectral lineshape calculation

3.2.1. Absorption coefficient. For the absorption coefficient calculation we take what is known as a Fourier approach, which represents, in fact, a generalization of the traditional approach accepted in the classical theory of spectral line broadening [13].

In the context of this approach, a transition amplitude $b(\omega)$ (in au) is given by

$$b(\omega) = -\mathrm{i}\int\sqrt{\frac{\Gamma(t)}{2\pi}}\exp\left[-\mathrm{i}\int(\Delta U - \Delta\omega)\,\mathrm{d}t\right]\mathrm{d}t \tag{5}$$

and can be interpreted as a Fourier transform of a transition dipole moment calculated with time-dependent quasimolecular wavefunctions. Here, $\Delta\omega$ is a frequency shift from the asymptotic position of a difference term at $R \to \infty$.

It should be mentioned that equation (5) suggests the following law for the conservation of normalization:

$$\int_{\omega_0}^{\omega} |b(\omega)|^2\,\mathrm{d}\omega = 1 - \exp\left(-\int_{t_0}^{t}\Gamma(t)\,\mathrm{d}t\right). \tag{6}$$

Equation (6) is a convenient additional control over the numerical spectral calculations carried out, because the values $\omega_0(t_0)$ and $\omega(t)$ are finite in specific calculations whereas, according to the physical meaning of the problem, the integration limits are infinite.

Note that we can neglect the non-adiabatic transitions between the considered states during the collision; this is because of the non-adiabaticity parameter of the problem $\xi^* = \pi\Delta\epsilon/2\alpha v = 19.6 \gg 1$, and it corresponds to a pure adiabatic case. For more details, see [7, 11]. For the spectrum averaged over the impact parameters ρ and energies E of colliding atoms we have

$$\langle|b(\omega)|^2\rangle = \int_0^\infty \rho\,\mathrm{d}\rho\int_0^\infty E\mathrm{e}^{-E/kT}\,\mathrm{d}E\,|b(\omega)|^2 \tag{7}$$

assuming a Maxwellian distribution over the energies E.

The absorption coefficient γ^{ab} is calculated on the assumption that the radial velocity of atom movement v_R is a constant in the vicinity of a point R_0 which is the most significant region of the spectrum formation. In the theory of spectral line satellites, for instance, the position of the difference function extremum is often used as R_0 [1]. In our case, as in atomic collision theory, the centre of the non-adiabatic region is naturally taken as the point R_0 which is defined as

$$R_0 = \frac{1}{\alpha} \ln \frac{V_0}{\Delta\epsilon}. \tag{8}$$

Note that $R_0 = 7.0$ au in the case of $m = 0$ projection and $R_0 = 3.6$ au for $m = 1$. Next, the integration in (7) over the impact parameters ρ can be performed analytically by entering a new variable $E^* = E(1 - \rho^2/R_0^2 - U^*(R_0)/E)$ and integrating by parts [14]. Then the absorption coefficient γ^{ab} is conveniently expressed by the product of two factors:

$$\gamma^{ab}(\omega, T) = N(R_0, T)S(\omega, T) \tag{9}$$

$$N(R_0, T) = \frac{g(\Omega^*)}{g(\Omega)} p(\Omega)\pi\bar{v}R_0^2 \exp\left(-\frac{U^*(R_0)}{kT}\right) \tag{10}$$

$$S(\omega, T) = \frac{\lambda^2}{4} \exp\left(\frac{\Delta\omega}{kT}\right)\langle|b(\omega)|^2\rangle \tag{11}$$

where $\langle|b(\omega)|^2\rangle$ after analytical simplification will take the form

$$\langle|b(\omega)|^2\rangle = \int_0^\infty \mathrm{e}^{-x} \left| b\left(\omega, v_R = \sqrt{\frac{2kTx}{\mu}}\right)\right|^2 \mathrm{d}x. \tag{12}$$

Here, $\bar{v} = \sqrt{8kT/\pi\mu}$; $p(\Omega) = g(\Omega)/g(J)$ is the probability of the formation of quasimolecules with projection Ω in the ground state; $g(\Omega^*)$ (or $g(\Omega)$) is a statistical coefficient of the quasimolecular state with projection Ω^* (or Ω).

The first factor (10) depends upon only the parameter R_0, apart from the temperature T, and defines the spectrum intensity. The $S(\omega, T)$ factor (11) is frequency dependent and completely determines the shape of the spectral line. It is obvious that the factorization of the absorption coefficient by this means is very convenient for the purpose of comparison with the experimental data, because the factor $S(\omega, T)$ (11) represents the spectral profile in relative units, which is often given by measurements. Thus, to find a spectral lineshape, the averaged integral (12) needs to be calculated with the corresponding statistical factor (see (9)–(11)).

3.2.2. Forbidden transition.

Once again, we start by considering the case of the $\Omega = 0^+$ quasimolecular state. Namely, curve 1 in figure 2 (and also curve 1 in figure 3) shows the results of the absorption spectrum (absorption coefficient γ^{ab}) calculation for the asymptotically forbidden ($\Omega = 0^+$, 4s3d ^{1}D)–($\Omega = 0^+$, 4s^2 ^{1}S$_0$) quasimolecular transition. The spectrum was obtained using equations (9)–(12) and the results are in good agreement with the experimental data (curve 2 in figure 2) not only in shape, but also in absolute magnitude, which is an important point to note. It should be particularly emphasized that no fitting parameters were used in the calculation.

What are the physical reasons for the formation of a satellite of this shape? There are two. The first and main reason is the state interaction which leads to a rapid change of the quasimolecular radiative width. To demonstrate the influence of the changing radiative width

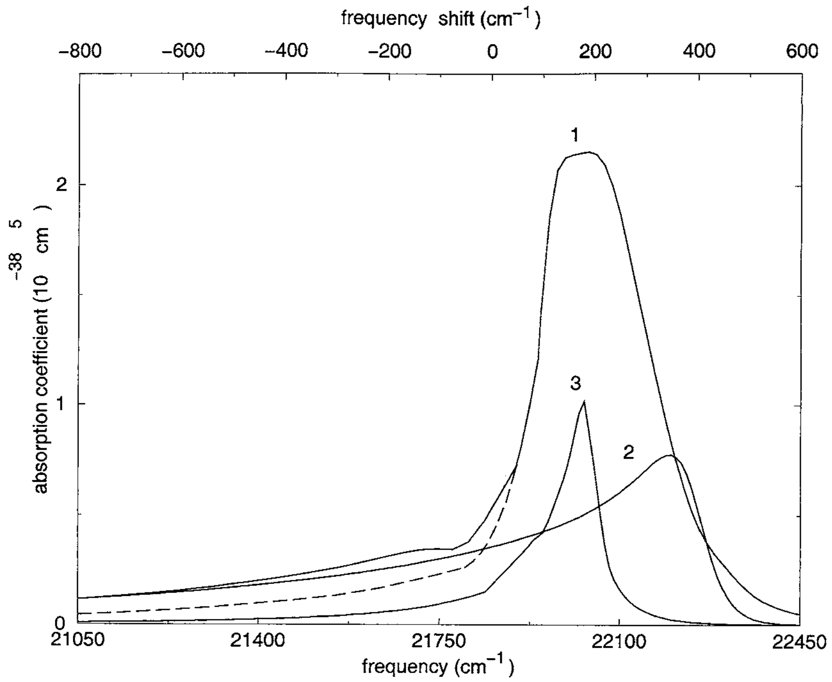

Figure 3. The absorption spectrum for the asymptotically forbidden $(\Omega = 0^+, 4s^2\,{}^1S_0) \rightarrow (\Omega = 0^+, 4s3d\,{}^1D)$ quasimolecular transition. Curve 1 shows the calculations in the semiclassical Fourier approach averaged over the impact parameters and the energies of colliding particles (the broken curve is the same, but with substitution of $R_0 \rightarrow R_c$); curve 2 is the spectrum calculations in the Fourier approach with the use of an exponential approximation for the difference potential curve (dotted curve in figure 1(*b*)); curve 3 demonstrates the spectrum calculations by the UFC formula given in [1].

on satellite formation, the results of the calculation in the Fourier approach with the use of the monotonic exponential function as a difference potential (dotted curve in figure 1(*b*)), are given by curve 2 in figure 3. The model approximation makes it possible to exclude the extremum of the difference function from consideration. One can clearly see that this approach describes the formation of the maximum near the forbidden atomic line, but its shape and position ($\Delta\omega_m = 340$ cm^{-1} to the blue region of spectrum) differ both from the experiment and from the previous accurate calculation in the Fourier approach (curve 1 in figures 2 and 3). Another reason for the satellite formation is the extremum in the difference potential curve. However, if we restrict ourselves to considering the mere influence of the extremum on spectrum formation, this approach also yields unsatisfactory results. To provide support for this view curve 3 in figure 3 demonstrates the spectrum calculation by the UFC formula given in [1] using the actual difference potential curve (figure 1(*b*)). The formula should be multiplied by $\Gamma(R_c)$, where R_c is the position of the Condon point. The comparison reveals that the UFC approach ignores the rapid changing of the radiative width. This method leads to a closer position of the spectral line maximum ($\Delta\omega_m = 180$ cm^{-1} to the blue region of spectrum), but its absolute intensity and form are still inadequate.

Thus, a consequence of the above discussion is that the Fourier approach succeeded in spectrum calculation, taking into account simultaneously both the occurrence of the extremum in the difference potential curve and the rapid changing of the radiative width. It is just this

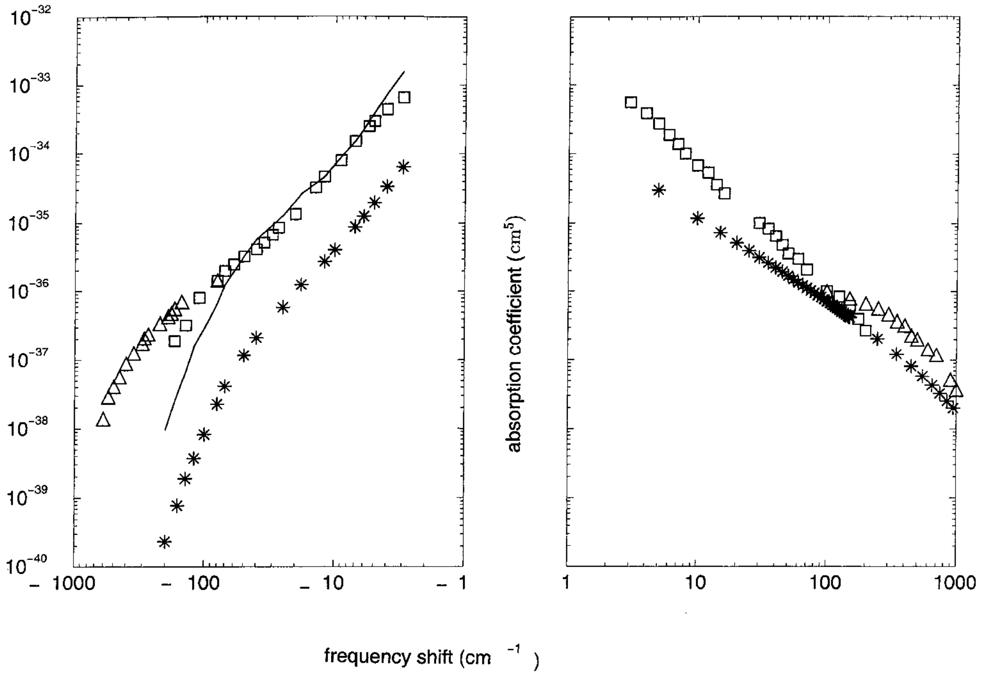

Figure 4. The absorption spectrum for the asymptotically allowed $(\Omega = 0^+, 4s^2\,{}^1S_0) \rightarrow (\Omega = 0^+, 4s4p\,{}^1P)$ quasimolecular transition. Stars, calculations in the semiclassical Fourier approach averaged over the impact parameters and the energies of colliding particles (the full curve is the same, but with $R_0 = 15$ au); triangles, experimental data for the spectrum; squares, experimental data of [15].

calculation which is presented by curve 1 in figures 2 and 3. We can refine the description of the spectrum in the region of real Condon point existence by replacing the fixed parameter R_0 by a current value of the Condon point R_c for every frequency. The corrected part of the spectral line using equations (9)–(12), but substituting a factor $N(R_c, T)$ for $N(R_0, T)$ in equation (10), is shown by the broken curve in figures 2 and 3.

Normalization of integral (6) over the spectrum obtained in the semiclassical Fourier approach for the case of the forbidden $(\Omega = 0^+, 4s^2\,{}^1S_0) \rightarrow (\Omega = 0^+, 4s3d\,{}^1D)$ quasimolecular transition (curve 1 in figures 2 and 3) comes out to

$$\int_{\omega_0(t_0)}^{\omega(t)} |b(\omega)|^2\,d\omega = 5.02 \times 10^{-6} \tag{13}$$

and the transition probability calculated from equation (6) gives us the following value:

$$1 - \exp\left(-\int_{t_0}^{t} \Gamma(t)\,dt\right) = 5.2 \times 10^{-6}. \tag{14}$$

One can see that the law of normalization conservation (6) is good within the accuracy of the analysis, the probability of the forbidden transition is of the order of 10^{-6}, so that for such small values of probability it is seen that the resulting values, (13) and (14), agree closely.

Note that for the case being studied, the contribution of the second allowed quasimolecular transition $(\Omega = 1, 4s3d\,{}^1D)$–$(\Omega = 0^+, 4s^2\,{}^1S_0)$ to the spectrum is insignificant, because the main part of the spectrum is formed in the blue forbidden region. What is more, the non-diagonal matrix element of interatomic interaction for the $\Omega = 1$ pair is six times less than for the $\Omega = 0+$ case and we can neglect the transitions to the $\Omega = 1$ state for the red wing of the spectrum as well.

3.2.3. Allowed transition. For the (4s4p ^{1}P)–(4s^2 ^{1}S$_0$) transition allowed in the atomic limit, both pairs of interacting quasimolecular states with $\Omega = 0^+$ and $\Omega = 1$ were treated simultaneously. However, it is clear from the difference potential curve that the inclusion of the ($\Omega = 1$, 4s4p ^{1}P)–($\Omega = 0^+$, 4s^2 ^{1}S$_0$) quasimolecular transition is essential for the red wing of the spectrum only, whereas its contribution to the blue wing is insignificant. The stars in figure 4 show the overall absorption spectrum obtained by equations (9)–(12), also considering the ($\Omega = 0^+$, 4s4p ^{1}P)–($\Omega = 0^+$, 4s^2 ^{1}S$_0$) and ($\Omega = 1$, 4s4p ^{1}P)–($\Omega = 0^+$, 4s^2 ^{1}S$_0$) quasimolecular transitions.

We note that the obtained spectrum correlates well with the experimental data (squares and triangles in figure 4) in shape for both wings of the spectrum, while the calculated intensity of the spectral line is much lower than that of the experimental one, in particular in the red wing of the spectrum. The reason for such a difference between the calculated and observed spectral intensity is that for the red wing calculation we use a fixed R_0 parameter in the $N(R_0, T)$ factor (see equation (10)), because there are no real Condon points R_c in this region. So, if a good fit of the calculated spectrum intensity to the experimental data is required, $R_0 \simeq 15$ au is used as a parameter under the $N(R_0, T)$ factor calculation (see the full curve in figure 4). Thus, in the red wing of the spectrum we supply a reliable calculation for the spectral lineshape, i.e. for the $S(\omega, T)$ function computation. For the blue wing of the spectrum the agreement between the calculated results and the experimental results is better, including the spectral line intensity. This is due to the use of the corrected factor $N(R_c[R_0 \to R_c], T)$ in the blue wing calculation of the allowed transition spectrum, similar to the refinement of the red wing for the forbidden transition spectrum.

The semiclassical Fourier approach suggested describes a full contour of the spectral line, including the classically forbidden part of the spectrum, which is beyond the reach of quasistatic calculations, and a central Lorentzian part as well (we do not include the central part of the spectrum in figure 4 for reasons of scale). For the case of the asymptotically allowed ($\Omega = 1$, 4s4p ^{1}P)–($\Omega = 0^+$, 4s^2 ^{1}S$_0$) transition it makes it possible to calculate the normalization integral (6) over the spectrum obtained in the semiclassical Fourier approach. The results of the normalization integral calculation for this case are

$$\int_{-\infty}^{\infty} |b(\omega)|^2 \, d\omega = 0.994. \tag{15}$$

It should be stressed that the intensity of the allowed spectral line differs from the forbidden one by six orders of magnitude. For this case, the spectrum measurements have been carried out using the same procedure for both of these spectral line types, and the spectrum calculations have followed a unified approach which spans six orders of the spectral intensity change.

4. Conclusions

In conclusion, let us sum up the basic results obtained. Using a single experimental set-up we performed absolute measurements of spectral line profiles for both allowed (4s^2 ^{1}S$_0$) → (4s4p ^{1}P) and forbidden (4s^2 ^{1}S$_0$) → (4s3d ^{1}D) transitions. The calculations follow the unified approach based on the Fourier transformation which allows us to calculate the spectra of both asymptotically allowed and forbidden quasimolecular optical transitions and to describe all fundamental peculiarities of quasimolecular emission spectra including the regions of the far wings, extrema and central part of the spectral line. The spectra obtained in the semiclassical

Fourier approach are averaged over the impact parameters ρ and energies E of the colliding atoms. For the case of the forbidden $(4s^2\,{}^1S_0) \rightarrow (4s3d\,{}^1D)$ transition it makes it possible for the first time to perform a direct comparison between the calculated spectral line and the experimental one, not only in shape but also in absolute magnitude. A good accord between theory and experiment lends support to the validity of the Fourier approach for the description of forbidden and allowed transitions produced by the interaction with an atom of buffer gas.

As mentioned above, the semiclassical Fourier approximation permits an extension of the approach accepted in the classical theory of spectral line broadening and correlates well with the rigorous, but model, treatment of [16, 17]. In particular, [16] shows that the Fourier approximation corresponds to the impact parameter method in collision theory, where the atom movement is treated classically, but the electronic transitions are described within the framework of quantum mechanics. The quantum approach to nuclear movement is usually essential for colliding particles approaching at low velocity and also for the description of light particle scattering [18].

Some theoretical research [19, 20] has been devoted to spectral calculations of quasimolecular optical transitions at the classical trajectories within the framework of the Fourier approach under discussion. However, the method proposed in these papers for the numerical calculation of spectra has a number of essential practical disadvantages. Firstly, for the case of asymptotically allowed quasimolecular transitions, when the fast-oscillating integral (5) for a transition amplitude $b(\omega)$ is calculated, the central Lorentzian part of the spectral line profile, which is the most cumbersome for the calculations, is expelled by artificial means in [19,20]. Only the wings of the spectral line adjacent to the central Lorentzian part of spectrum can be calculated using this approach, but the Lorentzian part of the spectrum contains the main portion of the spectral intensity. Thus, this approach gives us no means of carrying out the normalization of the spectra of the allowed quasimolecular optical transitions in the atomic limit; therefore, the method is unsuitable for the unified spectral line calculations for both asymptotically forbidden and allowed quasimolecular transitions. The Fourier approach used in this paper is free from the limitations outlined.

Acknowledgments

The research has been performed through RFBR grant N99-03-33168a and INTAS grant N99-00039. EB gratefully acknowledges the support of The Royal Society, NATO and The Foreign and Commonwealth Office Chevening Fellowship during her stay in Belfast.

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