Predicted Fluorescence Mechanism in Highly Isolated Molecules: The Poincaré Fluorescence

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(Received 29 October 1987)

We predict a completely new behavior of fluorescence for large- or intermediate-size molecules which are highly isolated (e.g., in the interstellar medium). After a UV absorption, the energy decay by IR emission alone is very slow ($\simeq 3$ s). The system evolves at constant energy during a long time period in its phase space, and unusual phenomena can occur. We infer an inverse internal conversion and a resulting recurrent fluorescence that we propose to name Poincaré fluorescence. Such a behavior seems quite universal and has characteristics markedly different from the usual fluorescence.

PACS numbers: 33.50.−j, 98.40.Ct, 98.40.Kb

The possibility of inverse internal conversion (IIC) has been proposed in the past[1,2] but has never been evidenced unambiguously in the laboratory. We show here that interstellar conditions are appropriate for such a process and predict a new fluorescence behavior.

In 1984, strong indications were given[3] for the presence of large (20-50 atoms) polycyclic aromatic hydrocarbon (PAH) free molecules in the interstellar medium, and since that time the research field has been very active.[4] The characteristic times of interaction of these molecules with their surroundings are remarkable. They absorb ultraviolet (UV) photons, cool by infrared (IR) emission, and have collisions with the ambient interstellar gas with typical times,[5] in a reflection nebula, $t_{\mathrm{UV}} = 3\times10^4$ s, $t_{\mathrm{IR}}^{\mathrm{cooling}} = 3$ s, $t_{\mathrm{coll}} = 5\times10^5$ s, respectively. The collision time, when compared with that in condensed phase experiments (10^{-12} s) or in jet experiments (10^{-6}-10^{-3} s), indicates that *the space "laboratory" offers impressive isolation conditions.* As a result, after the absorption of an UV photon the only route for molecular deexcitation, besides fluorescence, is slow IR emission. The molecule then remains excited for a time much longer than in usual laboratory conditions. In this paper, we take advantage of this new hierarchy of times and study physical processes that are usually neglected but can now become dominant. We consider the case of ions because PAH's are expected to be largely ionized[6] in the regions which are presently best observed (reflection nebulae, planetary nebulae, etc.), but our derivation can easily be extended to neutral species and radicals.

Figure 1 shows the energy-level scheme of ion states (D_i,U_i) with their electronic part (D denotes doublet) and vibrational part (energy U_i). The processes following the absorption of an UV photon are reported. They have been extensively described[7] and are only briefly summarized with an indication of their characteristic times. The UV absorption transition (D_0,U_0) to (D_n,U_n) and the other transitions are followed by rapid internal vibrational redistribution (10^{-12}-10^{-10} s) which allows the use of statistical physics.[8] From (D_n,U_n) the molecular ion undergoes fluorescence transitions ($\simeq 10^{-7}$ s) or internal conversion (IC) ($\simeq 10^{-12}$-10^{-8} s) to lower electronic states (D_p,U_p) until it arrives at the ground electronic state D_0 with a high vibrational energy. We have omitted the electronic levels with different multiplicity (quartets,...) for the sake of simplicity and because they do not have a conceptually essential role in ions.[9]

The IC, e.g., $(D_1,U_1)\rightarrow(D_0,U_0)$, is usually considered as irreversible because the density of states $\rho(U)$ is a rapidly increasing function of the vibrational energy $(U_0 > U_1)$, providing a larger phase-space volume in the final state (Fig. 2). However, this conclusion must be considered in greater detail for a system that remains a long time at the same energy. Provided that the ion has an ergodic behavior (statistically uniform occupancy of the available phase space), statistical physics specifies that the time spent in (D_1,U_1) or (D_0,U_0) is proportion-

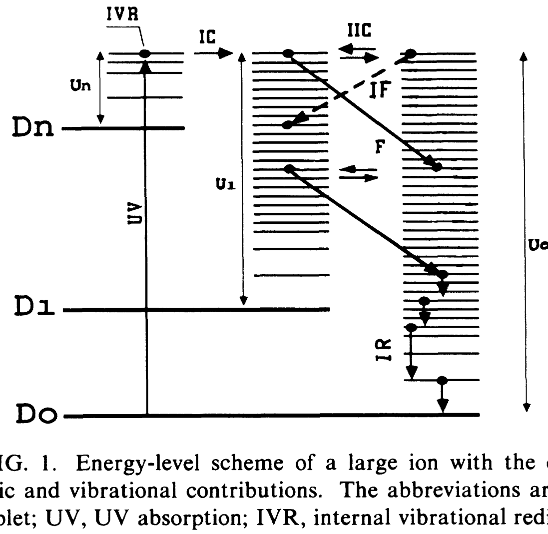

FIG. 1. Energy-level scheme of a large ion with the electronic and vibrational contributions. The abbreviations are D, doublet; UV, UV absorption; IVR, internal vibrational redistribution; IC, internal conversion; IIC, inverse internal conversion; F, fluorescence; IF, inverse fluorescence; IR, IR emission.

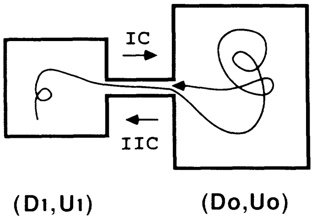

FIG. 2. Scheme of the isoenergetic evolution of the system in its phase space.

al to the density of states:

$$t_1/t_0=\rho(U_1)/\rho(U_0). \quad (1)$$

The function $\rho(U)$ can be calculated explicitly in the harmonic approximation if the molecular vibrational modes are known. This can be done by exact state counting or by the use of an analytic approximation such as that given by Whitten and Rabinovitch[10]:

$$\rho(U)=(U+aE_z)^{s-1}/\left[s!\textstyle\prod_j h\nu_j\right], \quad (2)$$

where $h\nu_j$ are the energies of the modes, s and E_z are their number and total zero-point energy, respectively, and a is a correction factor ($0<a<1$) that varies with U according to an empirical law given in Ref. 10. For an absorbed energy U_0 and a first excited electronic state D_1, at ΔE above the ground state, $\Delta E=E(D_1,0)-E(D_0,0)$, the ratio of the times spent in the (D_1,U_1) and (D_0,U_0) states is given by (1), with $U_1=U_0-\Delta E$. Its strong dependence on U_0 is reported in Fig. 3(a). As expected, this ratio is small, but it is not infinitely small which would correspond to irreversible transition from D_1 to D_0. This implies that the system can go forth (IC) and back (IIC) between the two states D_1 and D_0 at rates k_{IC} and k_{IIC}, respectively (Fig. 2). In usual laboratory conditions, the second process is negligible because, whenever in state (D_0,U_0), the system rushes down the vibrational ladder by thermal coupling with the surroundings (condensed phases) or is not observed for a long enough time (jet experiments).

This special behavior of isolated species has important consequences on their fluorescence emission. During each excursion in D_1, the ion has a probability $y_F=k_F/(k_F+k_{\mathrm{IC}})$ to emit a visible photon. Usually, when the system has been prepared in D_1 (or D_n), only the first occurrence of this process is important because the ion rapidly cascades down the vibrational ladder as soon as D_0 is reached. In the situation of high isolation, the system oscillates many times between D_0 and D_1 and the *cumulated fluorescence emissions* from D_1 can be important, leading to an effective rate $k_{\mathrm{eff}}=y_Fk_{\mathrm{IIC}}$. In the unrealistic limit of no other cooling, all the energy would have to be released through such a channel. For $k_F \ll k_{\mathrm{IC}}$, as is always the case when U_1 is reasonably large,

$$k_{\mathrm{eff}}=k_Fk_{\mathrm{IIC}}/k_{\mathrm{IC}}=k_F\rho(U_1)/\rho(U_0). \quad (3)$$

The second part of Eq. (3) results from the application of detailed balance.

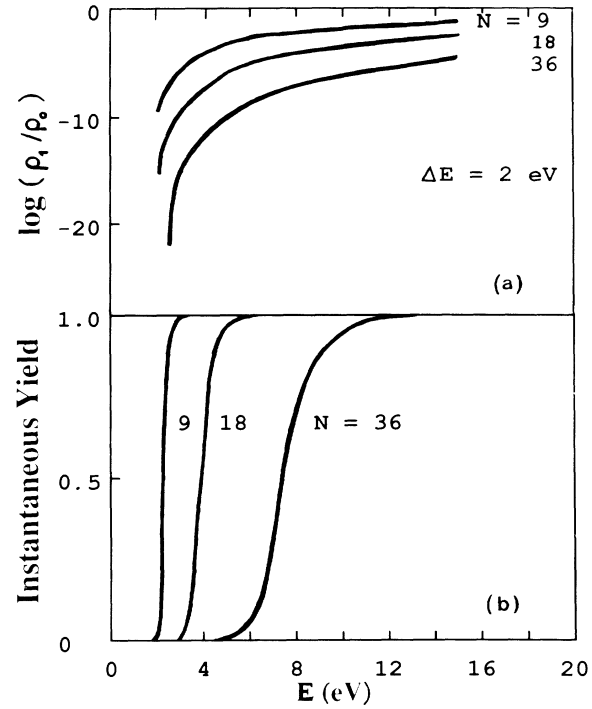

FIG. 3. (a) Ratio of the densities of states in the D_1 state (ρ_1) and in the D_0 state (ρ_0) vs the total energy (E) of the ion with use of Eq. (2). The vibrational energies of the states are $U_1=E-\Delta E$ and $U_0=E$, respectively, where ΔE is the energy of the 0-0 transition between D_1 and D_0. N is the number of atoms in the ion. (b) Resulting instantaneous fluorescence yield for the following molecular parameters: $k_F=3\times10^7\ \mathrm{s}^{-1}$ (an upper limit), $t_{\mathrm{IR}}^{\mathrm{cooling}}=3$ s, $\Delta E=2$ eV. At low energy, the ion relaxes emitting IR vibrational photons, and at high energy, emitting visual fluorescence photons.

This new fluorescence can be named "recurrent fluorescence" or "Poincaré fluorescence" as a tribute to the work of Poincaré on the dynamics of systems in their phase space.[11] We shall retain the latter designation, but it should be noted that the system returns to D_1 *long before having accomplished a whole Poincaré cycle* (Fig. 2). Expression (3) for k_{eff} can also be derived by consideration of an ensemble of ions with a given internal energy : It is k_F times the fraction of the population in D_1. The ratio of populations in D_1 and D_0, which is equal to the ratio of times spent in these states, is actually given by the ratio of densities of states $\rho(U_1)/\rho(U_0)$ [Eq. (1)] because the fluorescence decay is slow enough not to perturb significantly the kinetic equilibrium between IC and IIC ($k_F \ll k_{\mathrm{IC}}$)

In high-isolation conditions, provided the ergodic assumption holds, the above arguments are straightforward. So, let us consider the validity of this assumption. The equivalence between a kinetic model and the quantum mechanical treatment has been shown in Ref. 1. Moreover, Eq. (3) is identical to Eq. (V-18) of Ref. 2, also derived from quantum mechanics. This justifies the use of the ergodic assumption when U_1 is large enough to ensure complete overlap of the vibrational levels (fast internal vibrational redistribution).

The decay of the total energy ($E = U_0$) of the ion proceeds either by fluorescence or by IR emission. With use of (3) and $\rho_1 \ll \rho_0$, the energy-decrease rates through these channels are, respectively,

$$(dE/dt)_F = -k_{\rm eff}\Delta E, \quad (dE/dt)_{\rm IR} = -k_{\rm IR}E, \qquad (4)$$

with $k_{\rm IR} = 1/t_{\rm IR}^{\rm cooling}$.

An *instantaneous fluorescence yield* can be defined as the E-dependent ratio $(dE/dt)_F/[(dE/dt)_F + (dE/dt)_{\rm IR}]$. It is reported in Fig. 3(b) as a function of the energy E of the ion for typical values of the molecular parameters. From these curves, it appears that the instantaneous Poincaré fluorescence yield increases from zero to essentially 1 as the ion internal energy increases, pointing out the importance of the process. The energy and the width of the transition between the two regimes depend on the molecule size and on ΔE: The smaller the molecule and ΔE, the lower and the more abrupt the transition. Such a yield is mainly governed by density-of-states factors. Consequently, *the behavior of Fig. 3(b) is quite universal:* Besides the dependences mentioned above, there is little influence of features specific to the system such as the fluorescence rate k_F. For instance, a ten-times decrease of k_F would only shift the curve for $N = 9$ atoms by 0.2 eV.

For a molecule having absorbed one photon with energy $h\nu_{\rm UV}$, the *quantum fluorescence yield* (Z) is the number of fluorescence photons which are emitted during the energy decay process. It can be calculated in a Monte Carlo simulation considering at each energy step the two possible decay channels. Figure 4 shows such a quantum yield versus the energy of the absorbed photon. We have simplified the description by using a single fluorescence photon energy ($h\nu = \Delta E$); a broader fluorescence spectrum would smooth the curve steps. *A striking difference between Poincaré fluorescence and usual fluorescence is the possibility of quantum yields larger than 1.* When the absorbed energy is high enough, several fluorescence photons can be emitted during the cascade, because the molecule comes back several times into the D_1 state. This is in contrast to the usual fluorescence where the quantum yield (y_F) is determined by the initial competition between fluorescence and IC and is less than unity.

It should be mentioned that another fluorescence mechanism has been suggested by Leach[12] also as a consequence of the long stay of the system at high energy: the *inverse fluorescence* reported in Fig. 1. Energetically, the system can make a transition from a (D_0, U_0) state to a lower energy state (D_1, U_1'), emitting a photon. The corresponding Franck-Condon factor is certainly small because the vibrational states characterized by U_0 and U_1' are very different, but the corresponding transition rate should be compared with the slow IR radiative cooling rate (0.3 $\rm s^{-1}$) and not with the fast IC rate as for usual fluorescence. Future estimates of these factors are required to decide whether this is an important process. Remarkably, the inverse-fluorescence photon energy is *not* necessarily close to that of the usual fluorescence $(D_1,0) \rightarrow (D_0,0)$. This would be in contrast to the usual (and Poincaré) fluorescence and would probably give very broad emission bands or even a continuum.

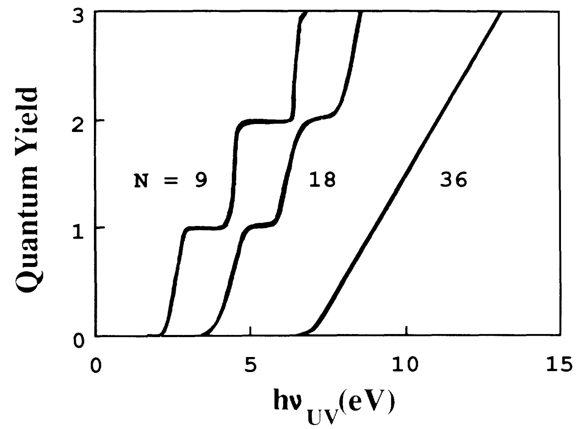

FIG. 4. Quantum yield (Z) of the Poincaré fluorescence vs the energy of the absorbed UV photon. In contrast with usual fluorescence, Z can be larger than 1, corresponding to *the emission of several photons of fluorescence for one absorbed photon.* Curves are calculated for different numbers of atoms in the species and for $\Delta E = 2$ eV.

If molecules can be isolated for a long enough time, the Poincaré fluorescence and the IR emission should be observable in the laboratory, especially with middle-size molecules. This is a challenge for experiments in the future.

The Poincaré fluorescence may be the explanation of the red-light luminescence which is observed from many interstellar regions.[13] This point and other astrophysical implications will be discussed in a forthcoming paper.

We are indebted to A. Beswick who first pointed out to us the eventuality of IIC during the interdisciplinary meeting of Les Houches (in February 1986) on PAH's and Astrophysics. It is also a pleasure to thank J. Jortner, S. Leach, V. Bondibey, J. L. Fave, A. Tramer, and A. Omont for important and enthusiastic discussions on this process. The Groupe de Physique des Solides de l'Ecole Normale Supérieure is Unité Associé No. 17 du Centre Nationale de la Recherche Scientifique.

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