Theory of multiphoton dissociation of polyatomic molecules under the action of an infrared laser field

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Under the action of an intense infrared laser field, polyatomic molecules will undergo instantaneous dissociation which is shown by experiment to be not a thermal one but a photo-dissociation induced by multiphoton absorption. We have worked out a theory about this phenomenon. In the physical model suggested here the multiphoton photo-dissociation process may be represented in the form of uni-molecular reaction i.e.

A (molecule) + W (many photons) $\longrightarrow$ A* (excited molecule) $\longrightarrow$ B+C (dissociation).

After a molecule has absorbed photons, because of coupling between vibrational modes this energy of the molecule is distributed on many vibrational modes but the energy of each mode is not too great. After a certain time interval the "interference" between the various modes of the excited molecule results in "deformation" of one of the bonds beyond the breaking limit, hence giving rise to dissociation. The average length of this interval determines the rate of disscoiation.

The excitation of a polyatomic molecule which is approximated by a multidimensional anharmonic oscillator system includes two processes. In the first place, the external field excites a near-resonance mode. Secondly, this mode excites other modes through anharmonic coupling with them.

The anharmonic oscillator in an external field has been calculated and its time evolution operator U (t, o) is given below to the first approximation:

$$U(t,o) \approx U^{(1)}(t,o) = e^{-i\omega t(a^+ a + \frac{1}{2})} e^{A(t) + \xi_1(t)a^+} e^{-\xi_1^*(t)a}$$

This implies that the state of this one-dimentional oscillator is a "coherent state", that is to say the probability of the oscillator being in the state $|n>$ at any instant t is

$$P_n(t) = e^{-|\xi_1|^2} |\xi_1|^{2n}/n!$$

This is a Poisson distribution, where $\xi_1(t)$ satisfies a non-linear equation and may be solved by the Krylov-Bogoliubov asymptotic method. Digital calculation for a single mode gives the following results:

(1) For the SF_6 molecule the calculation shows that the "threshold value" (i.e. the value of light intensity under which the molecular dissociation rate increase rapidly) actually was close to a few tens of MW/cm^2 of light intensity (or a few of J/cm^2 of energy).

(2) Theoretical calculation of the frequency "red-shift" is in agreement with ex-

perimental observation; for SF_6 the peak of the curve representing the relationship between photodissociation and light frequency was shifted towards the long wavelength end by several cm^{-1}.

(3) Theoretical calculation of the time required for an oscillator to be excited from a very small (≈ 0) amplitude to its maximum amplitude is $10^{-10} \sim 10^{-11}$ second, which explains the "instantaneous" nature of the experimental phenomena.

A further calculation has been made for the problem of forced coherent excitation of multimode molecular system. So long as there is a near "Fermi resonance" (i.e. $\sum_i n_i \omega_i \approx 0$, where n_i is an integer), energy transfer between the various vibrational modes is fairly rapid, of the order of 10 ps in our calculation. These excited vibrational modes are also "coherent states", and as a result of the lower order of Fermi resononce, the vibrational modes involved have already been effectively excited. In our calculations, we have employed Slater's uni-molecular reaction model to discuss the dissociation rate of polyatomic molecules and have obtained results which are essentially in agreement with experiments.
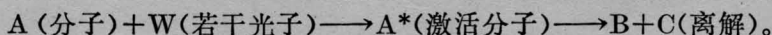
在强红外激光场作用下多原子
分子的多光子离解理论

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在强红外激光场作用下，多原子分子将发生瞬时离解。实验表明，这种离解过程不是热离解过程，而是由多光子吸收引起的光致离解过程。我们提出了一个理论模型用以解释有关的实验现象。在我们的理论模型中，多光子离解过程可以表示成下列的单分子反应形式：

A（分子）＋W（若干光子）──→A*（激活分子）──→B＋C（离解）。

一个分子吸收光子以后，由于振动模式之间的耦合，这分子的能量很快地转移到其它振动模式上去，而每个模式的能量不是很高。激活分子的各个模式之间发生"干涉"，经过一定时间，当分子某一个键上结聚的能量超过该键的破坏极限时，分子就离解，离解速率由上述平均时间决定。

多原子分子可近似地看成一个多维的非简谐振子系统，它的激活过程分成两步。首先，与外场的频率相近的模式被共振地激活。然后，通过激活模式与其它模式之间的非线性耦合，再把其它模式激发起来。

一个非谐振子在外场作用下的激发过程可以用时间演化算符 $U(t,0)$ 描述，在一级近似下

$$U(t,0) \approx U^{(1)}(t,0) = e^{-i\omega t(a^+a+\frac{1}{2})} e^{A(t)+\xi_1(t)a^+} e^{-\xi_1^*(t)a}$$

上式表明，一维振子是"相干态"，在时刻 t 处在 $|n>$ 态的几率为

$$P_n(t) = e^{-|\xi_1|^2} |\xi_1|^{2n}/n!$$

这是 Poisson 分布，式中 $\xi_1(t)$ 满足一个非线性方程，可用 Krylov-Bogoliubov 渐近方法求解之。我们对单模振子进行了数值计算，理论结果如下：

（1）对于 SF_6 分子，其离解"阈值"（即分子离解率随光强急剧增加时光强的数值）接近于光强为数十兆瓦/厘米²，或相应的能量为数焦耳/厘米²。

（2）对于 SF_6 分子，频率红移的理论结果约为几个厘米⁻¹，与实验基本符合。

（3）一个振子从非常小的振幅激发到极大值所需时间（激发时间）理论上约为 $10^{-10} \sim 10^{-11}$ 秒，这与实验上分子离解的瞬时性现象是一致的。

我们进一步计算了由多个振动模式组成的多模分子系统的相干激发问题。只要振动模式之间存在"近费米共振"（即 $\sum_i n_i\omega_i \approx 0$，$n_i$ 为整数），振动模式之间的能量转移时间就会较快，在我们的计算中约为 10 微微秒量级。这些激发振动模式也是"相干态"。于是，通过"近费米共振"，各振动模式有效地被激发起来。最后，我们用 Slater 的单分子反应模型计算了多原子分子的离解速率，得到了与实验基本一致的理论结果。